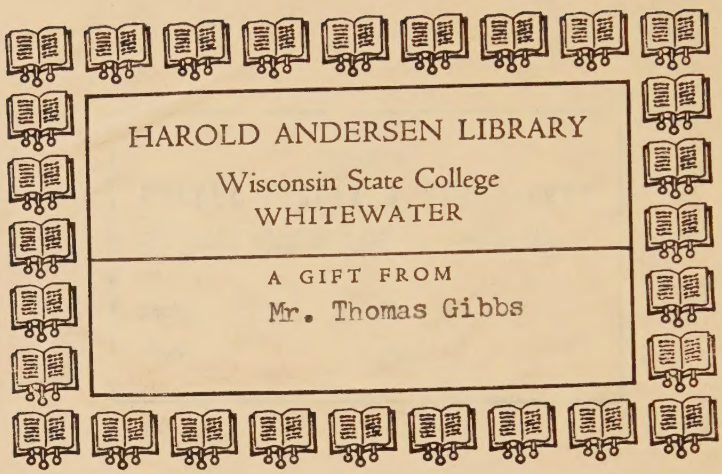
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PRINCIPLES OF ELECTROPLATING AND ELECTROFORMING (ELECTROTYPING)

PRINCIPLES OF ELECTROPLATING AND ELECTROFORMING

(ELECTROTYPING)

BY

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SECOND EDITION
FOURTH IMPRESSION

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PREFACE TO THE SECOND EDITION

In the first edition of this book an effort was made to serve both platers and chemists, by bringing to the former some knowledge of chemistry and to the latter some knowledge of plating. It was, of course, realized that to cover these fields fully in so limited a space was impossible, and hence there were many intentional omissions of facts or principles that might have found place in a more comprehensive treatise.

Similarly in the revision of this book, the effort has been, not so much to make it more complete and comprehensive, as to make every statement in it as accurate as present knowledge permits, and especially to explain all the facts and principles in the clearest and simplest manner. Such large additions as have been made, *e.g.*, the chapter on chromium plating, are confined to those phases of the subjects which are of present or probable future importance to the plating industry.

No attempt has been made to include a complete bibliography in this or the first edition. The references that are included are chiefly for the purpose of calling attention to recent accessible articles in English, in many of which the previous literature is summarized. For reference to foreign papers the reader is referred to the scientific publications of the authors and their associates at the Bureau of Standards.

During the six years that have passed since the first edition appeared, there have been many changes and much progress in the plating industry. The platers have come to a fuller realization of the value and importance of chemistry and are attending classes more enthusiastically than ever before. Many more chemists have been employed for the study and standardization of plating processes. Manufacturers of plating materials and supplies are engaged in researches to improve their products. Industries that involve much plating, notably the automobile industry, are demanding a higher quality in order to meet a corresponding demand on the part of the purchasing public.

The continuation and extension of the progress brought about by these activities requires a more general understanding, and

especially a more effective correlation, of the principles and practice of electroplating. That was and is the chief purpose of this book. In this second effort toward its accomplishment we have been greatly helped by the work of investigators in university and industrial laboratories, and by information and suggestions received from many chemists and platers. To all of these we desire to express our thanks and appreciation.

William Blum.
George B. Hogaboom.

Washington, D. C.
December, 1929.

PREFACE TO THE FIRST EDITION

During the past several years the authors have been associated with the investigation of electrotyping and electroplating processes at the Bureau of Standards. These studies have been carried out not alone to assist wherever possible other branches of the government service, but also to secure information useful to the manufacturing industries. In this field the Bureau has worked in close cooperation with the American Electroplaters' Society and the International Association of Electrotypers. In general, the results of specific investigations have been made public from time to time, through Government publications and by presentation in appropriate journals.

Through the close association thus gained with persons connected with the above industries, the authors have become convinced that before there can be any extended industrial application of the results of research work, there must be a more general recognition and application of the established and fundamental principles of the related sciences. This book has therefore been prepared not so much for the purpose of presenting the results of research, as of assisting those in the industry to understand and apply the results that have been or may be secured in various research and educational institutions.

A new word, "electroforming," has been employed in this book. It may be defined as "the production or reproduction of articles by electrodeposition." It is suggested as a substitute for the term "galvanoplasty," which has been occasionally used in English or American texts. It includes electrotyping, the reproduction of phonograph record matrices, and the manufacture of tubes and other objects by electrodeposition. The whole field of commercial electrodeposition is, then, covered by the four analogous terms, electrorefining, electrowinning,[1] electroplating, and electroforming.

[1] Electrowinning is a term frequently used for the electrolytic recovery of metals from solutions obtained by leaching ores, as, *e.g.*, in the production of electrolytic zinc.

For the information regarding general principles and processes the authors have drawn freely from various texts and journal articles. No attempt has been made to give a specific reference for each statement made, but a few important references upon each subject have been cited for the benefit of those desiring to study the literature of electrodeposition.

The authors are especially indebted to the Bureau of Standards for the privilege of using subject matter and illustrations from articles that have appeared previously from that Bureau, and of using in a few cases their unpublished data. The authors wish also to thank the American Electrochemical Society for the loan of cuts of illustrations which have appeared in their transactions.

For many of the facts and formulas of commercial processes, the authors are indebted to numerous electroplaters and electrotypers, especially the members of the American Electroplaters' Society, and of the International Association of Electrotypers. To their colleagues at the Bureau of Standards they are indebted for helpful advice and suggestions.

WILLIAM BLUM.
GEORGE B. HOGABOOM.

WASHINGTON, D. C.
January, 1924.

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PRINCIPLES OF ELECTROPLATING AND ELECTROFORMING

CHAPTER I

INTRODUCTION

Electrodeposition was for years conducted as an empirical art, using processes that were often considered secret. During the past ten years, however, there has been throughout the United States a definite movement toward the application of science. In this movement the American Electroplaters' Society, the International Association of Electrotypers and the American Electrochemical Society have taken active parts. Through meetings of the Electroplaters' Society and its various branches, and through classes conducted under its auspices, many electroplaters are acquiring a knowledge of the fundamental principles of chemistry and electricity, and are applying such principles in their daily tasks.

The desire to acquire and apply such knowledge is all too likely to express itself in the reading or study of only those topics which are immediately applicable to electrodeposition. Such a policy is short-sighted, because real progress, both for the individual and the industry, must depend upon a foundation of broad, even though elementary, principles of science. To acquire such a foundation, every electroplater should, if possible, pursue a regular course in elementary chemistry, conducted by an experienced teacher, as in the numerous evening technical schools. It is by no means essential that such a teacher should have any extended knowledge or experience of electrodeposition, although a slight acquaintance with the commercial processes will enable him to make the course more interesting and helpful through the use of familiar illustrations.

In bringing together some of the fundamental principles involved in electrodeposition, and explaining some of their applications in practice, the authors do not have in mind a textbook for such classes. Any good text on general chemistry will serve far better for this purpose. It is their desire, however, that this book may serve as a guide to teachers of such classes, by indicating some of the applications of science to electrodeposition, and may at the same time inspire progressive electroplaters and electrotypers to master those fundamental principles which are essential to any intelligent employment of science in these industries.

The many applications of electroplating in the production of military supplies during the World War, and the difficulties encountered both in meeting new problems and in standardizing well-known processes, emphasized to manufacturers the important relation of electroplating to the appearance and durability of their products. In consequence, chemists connected with large manufacturing plants were often for the first time called upon to assist in the solution of the electroplaters' problems. Not infrequently such cooperation between chemists and platers, even when cordial, was unsuccessful, principally because neither understood the language of the other. If there is to be any genuine progress in the electroplating industry during the next generation, there must be wherever possible, especially in large plants, hearty cooperation between the chemist and the plater; cooperation, because neither one can or should displace the other. It is hoped that this book will in some measure foster such cooperation and meet the need for a common language, firstly by expressing in simple terms the important scientific principles and data, and secondly, by crystallizing some of that large fund of empirical information which has been acquired by observant platers through years of experience. The scientist possesses no monopoly of truth. Persons desiring to conduct research upon electroplating should first become acquainted with the present practice and problems, and so far as possible view them through the eyes of the practical man. Having acquired that point of view, the chemist should by no means confine his methods of research to those which are familiar to, or applicable by, platers. Exhaustive or fundamental progress upon electroplating problems demands the application of the most advanced principles and methods of electrochemistry. And even in the field of analytical

chemistry, too often considered as exhausted, and hence neglected, there is need for genuine research of a high order, to secure simple or reliable methods for the analysis and control of plating solutions, such as the cyanide solutions which are so extensively used. The structure and physical properties of anodes and of the deposits must be studied and coordinated with their service. In this book no effort will be made to discuss in detail the methods to be employed in research, but it is hoped that by pointing out in various connections the needs and possible directions for research, work of this character will be stimulated.

It is, however, for the actual control and testing of plating solutions and deposits that the works' chemist is most likely to be called upon. With the great variety of products handled in the testing laboratory of a large plant, the chemist rarely has opportunity to study or develop methods especially suited for the analysis of plating solutions. To assist him, numerous methods, as used at present, are described which have been found to be simple and sufficiently accurate for control work. In general, these methods are given in outline, with only such directions as are required by an experienced chemist. At the same time sufficient details are included to permit a plater with some training in chemistry to carry out many of the tests under the supervision of a chemist. Except for a few simple titrations and colorimetric tests, it is useless, and in general unwise, for a plater without some systematic training to attempt to make analyses of the solutions, as the results are likely to be very inaccurate and misleading. It is possible, however, for a plater after brief instruction, to learn sufficient of the "mechanics of analysis" to enable him to make specific tests with an accuracy adequate for the maintenance of satisfactory working conditions. Even in such cases, however, contact with a chemist is desirable in order to check the standards and methods employed.

Sometimes practical platers, or persons who plan to become platers, express a desire for a book of "plating formulas." Such a book would no doubt have a certain value. If, however, a large number of formulas are given without any discussion of their applications or limitations, the practical plater is more likely to be confused than helped. It has therefore seemed to the authors that the industry will be benefited most by the collection of a few typical formulas, known to be in successful use for the various kinds of plating, together with such information

as is available regarding the favorable conditions of operation and the factors determining or limiting the usefulness of each process. With the present dearth of exact information it is necessary in some cases to make predictions rather than statements as to probable effects. Every effort has been made to distinguish in the text between statements based upon commercial practice, upon completed researches, and upon general considerations.

In the related field of electroforming, which includes electrotyping, the methods and principles of electrodeposition are so similar that it is felt desirable to include a discussion of this art, even though many of the details of operation are quite different. One reason for dealing with these two closely related industries in one text is the hope and belief that each may benefit by a consideration of the methods employed by the other.

It is, then, the hope of the authors that this book may be of interest and assistance to electroplaters and electrotypers, to teachers and students, to research and to works' chemists, and to manufacturers, and may serve to stimulate the application of science in the electroplating and electrotyping industries.

CHAPTER II

METHODS OF EXPRESSING CONDITIONS OF OPERATION

1. GENERAL PRINCIPLES

Reliable operation and control of any process, such as electrodeposition, which involves changes in the composition and form of matter, depend upon the measurement and knowledge of certain conditions of operation, such as the composition, density, or temperature of the solutions, the capacity of the tanks, the current density and voltage employed, and the thickness of the deposited metal. In measuring or recording such data it is customary in most commercial work to employ the ordinary or English units, the Fahrenheit scale of temperture, and the Baumé scale of density. In scientific work, including most of that conducted in works' laboratories, the metric units, Centigrade temperature scale, and specific gravity are generally used. It is highly desirable to bring about the general adoption of the more scientific units, which are much simpler to use. It is recognized, however, that even if the metric system were actually adopted in the near future, a considerable period would elapse before it could come into common usage. In this book, therefore, all important values will be expressed in both units, so as to be immediately useful both to chemists and to platers. The latter are urged to become as familiar as possible with the scientific units, in order that they may be better able to make use of the results of scientific investigations, and of such tests as may be conducted by chemists.

Before considering in detail the methods of expressing the results of any measurement, it is important to discuss at some length the principles of "relative accuracy" and "significant figures," since a disregard of these principles often leads both practical and scientific persons to misconceptions and to waste of time and energy. The first principle depends upon the fact that the various measurements which enter directly into any final result should be made with approximately the same degree

of relative accuracy. No measurements are absolutely accurate, owing to unavoidable errors in the calibration and use of any measuring instrument. Up to a certain point such errors may be reduced by definite precautions. The amount of care that is warranted depends entirely upon the use which will be made of the results. Thus, there is no advantage in measuring the dimensions of a plating tank to one-hundredth of an inch when we cannot adjust or maintain the height of the solution in the tank within one-quarter of an inch. Similarly, there is no advantage in measuring two of the tank dimensions with an accuracy of only 1 per cent, and the third dimension with an accuracy of one-tenth of one per cent, since the final result desired *i.e.*, the capacity of the tank, will be no more accurate than the least precise measurement.

For practical purposes we may assume that satisfactory results will be obtained if the composition of a plating solution is maintained constant to within 2 per cent (*i.e.*, 1 part in 50) of the actual concentration of each constituent. Any solutions requiring more accurate control than this are inapplicable for modern commercial plating. In the calculation of any actual result, such as the nickel content of a plating solution, a number of separate factors are involved, such as the volume of the solution (which in turn depends upon the length and width of the tank and the depth of the solution), the volume of the sample used in the analysis, and the weight of nickel obtained (or the number of cubic centimeters required for the titration). Since the accidental errors involved in some of these measurements may be in the same direction, and therefore cumulative, it is desirable to make the individual measurements with somewhat greater accuracy than is required for the final result. If, for simplicity, we assume that we desire to adjust the composition of a plating solution to within 2 per cent, an accuracy of 1 per cent (of the value concerned) is usually adequate for the separate measurements involved in the determination of the composition.

In expressing the results of such measurements, or of calculations based upon them, it is therefore useless to employ any more figures than are necessary to indicate an accuracy of about 1 per cent. Thus for the above purposes it is just as accurate, and far more convenient, to state that the volume of a plating solution is 235 gal. as to call it 235.36 gal., even though the calculations might indicate the latter volume. In other words, no more

"significant figures" should be employed than are justified by the accuracy of the measurements or by the use to which the results are to be put. By "significant figures" is meant those numerals which determine the relative accuracy of the value involved. Thus in the above illustration the value 235 gal. has three significant figures, while 235.36 gal. has five such figures. The first value indicates merely that the true volume is nearer to 235 gal. than it is to 234 or to 236 gal.; the latter value would indicate (assuming that its use were justified) that the true volume is closer to 235.36 gal. than to 235.35 or 235.37 gal. Similarly, a value of 28.7 oz./gal. of nickel sulphate has three significant figures, and is for practical purposes just as accurate as the value 28.676 oz./gal., which has five significant figures. In general, we may state that for this class of work it is sufficient to round off all the values involved to three significant figures. If in any given case a chemical analysis had shown that a solution contained (as based on the actual measurements involved) 214.47 g./l. of nickel sulphate, it should be reported as 214 g./l. If, then, this value is converted to oz./gal. (by multiplying by the factor 0.134) the actual result is 28.676 oz./gal., but the practical value is 28.7 oz./gal. (not 28.6 oz./gal).[1]

In general, in calculations of such data as the composition of plating solutions, the additions that may be required, the current density, the thickness of deposits, etc., the intelligent use of a slide rule will not only reduce the time required in making calculations, but will also tend to eliminate the use of superfluous figures. Several platers who have been initiated into the use of a slide rule have found it of great assistance to them. A few minutes' instruction and some practice will enable any intelligent plater to use a slide rule.

2. METHODS OF EXPRESSING TEMPERATURE

The thermometer usually employed in scientific work is the Centigrade thermometer, on the scale of which the freezing point of water is 0° and the boiling point of water (at a pressure of 1 atmosphere) is 100°, while on the Fahrenheit scale the corresponding points are 32° and 212° respectively. In general,

[1] Similarly, a statement that "10 c.c. of sulphuric acid is to be added to 10.0 c.c. of the plating solution" indicates that the measurement of the acid is only approximate, while that of the plating solution is accurate to at least 1 per cent.

preference will be given to the Centigrade scale, but in view of the prevalent use of the Fahrenheit scale, the values on the latter will also be included. The conversion of temperatures from one scale to the other can be readily accomplished by the use of simple formulas.

(*a*) To convert Centigrade to Fahrenheit temperatures, multiply the degrees Centigrade by 9/5 and add 32°.

Example.—To convert 20°C. to Fahrenheit:

$$\left(\frac{9}{5} \times 20°\right) + 32° = 68°\text{F.}$$

(*b*) To convert Fahrenheit to Centigrade temperatures, subtract 32° from the degrees Fahrenheit and multiply the remainder by 5/9.

Example.—To convert 77°F. to Centigrade:

$$(77° - 32°)\frac{5}{9} = 45° \times \frac{5}{9} = 25°\text{C.}$$

The relation between the two scales may be readily seen from Tables 1 and 2 in the Appendix.

3. METHODS OF EXPRESSING DENSITY OF SOLUTIONS

For testing the density of solutions either a Baumé (B. or Bé.) or a specific gravity (sp. gr.) hydrometer may be used. By the specific gravity of a liquid is meant the ratio of the weight of a given volume of the liquid to the weight of an equal volume of pure water, both the liquid and the water being at a definitely stated temperature. Most of the hydrometers used for commercial work in this country are graduated for a temperature of 15.6°C. (60°F.) for both the liquid and water. Such hydrometers are said to be graduated for $\frac{60°}{60°}$F. If, then, a certain solution has a specific gravity of 1.15, any definite volume of that solution at the above temperature weighs 1.15 times as much as does the same volume of water at that temperature. For the benefit of persons still using Baumé hydrometers, Tables 3 and 4 for the conversion of degrees Baumé to specific gravity and vice versa will be found in the Appendix.

To read a hydrometer, it should be floated in a glass cylinder or jar sufficiently wide that the hydrometer does not touch the sides. The true reading is the point at which the lower edge of the "meniscus" (*i.e.*, the curved surface of the liquid) crosses

the hydrometer stem. This is best observed by looking through the solution, with the eye just level with the meniscus. As many of the plating solutions are too deeply colored to permit reading through the solution, it is sometimes necessary to take the reading from above the solution. For most purposes the results so obtained are sufficiently accurate, especially if the cylinder containing the solution is fairly wide. For greater accuracy a correction can be made, based upon the difference in the readings of the hydrometer as viewed from above and below when immersed in pure water or any colorless aqueous solution of suitable density in a similar sized cylinder.

In the use of a hydrometer it should be borne in mind that the density should always be measured at approximately the same temperature (preferably that for which the hydrometer is graduated). It is also important to note that only in those cases where but one constituent (in addition to water) is present does the density of a solution indicate the composition. Thus for a solution containing only copper sulphate, the density at a certain temperature defines the concentration. If, however, one or more other constituents, such as sulphuric acid, aluminum sulphate, etc., are present in the solution, the density indicates (and then only approximately) merely the total concentration of material dissolved in the water. The use of a hydrometer is therefore not adequate to determine the composition of any plating solution containing more than one dissolved constituent. Its use is very helpful in indicating the extent of the losses of solution that may occur either by mechanical withdrawal or by leakage, provided the solution is always adjusted to the same level in the tank before making the measurement. In some cases—as in an acid copper solution (page 218)—a density determination, together with a simple titration, may yield an accurate analysis of a solution containing two dissolved constituents.

4. METHODS OF EXPRESSING COMPOSITION OF SOLUTIONS

Among the numerous advantages of the metric system may be mentioned the following: (*a*) The fact that the units are related in multiples of 10 greatly simplifies calculations; (*b*) the simple relation between the units of capacity and volume (1 l. is equal to 1 cu. dm. or 1,000 c.c.) facilitates the calculation of the capacity of tanks or vats; (*c*) the simple relation between the units of

weight, volume, and capacity (1 kg. is equal to the weight of 1 cu. dm. or 1 l. of water at its maximum density) renders very convenient the calculation of the weight of a given volume of water or of any liquid of known specific gravity. A complete list of the definitions and accurate tables of equivalents of the United States and metric units of weight and measure will be found in the Bureau of Standards Circular No. 47. The relations between the values most commonly used in this work will be found in Table 5 in the Appendix.

Wherever practicable, it is highly desirable to use the metric system in the actual plating operations. By the use of a meter rule (or a 60-cm. fourfold rule), a set of metric weights or a platform scale with metric graduations, and a suitable measure, holding, *e.g.*, 10 l., the metric system could be installed in a plant in a very short time.

In any case, if the plater is to make use of the results of analyses that may be made for him, or of results of plating investigations, it is necessary for him to become familiar with some metric units, and the methods of converting them into ordinary units. Wherever such conversions are necessary, it is preferable to make an entire calculation in metric units, and then to convert to ordinary units, rather than to mix the units and calculations. Efforts toward short cuts, such as the use of an "assay gallon"[1] (*i.e.*, 13.4 c.c. of solution), so that the results may be obtained directly in terms of oz./gal., are likely to lead to confusion, and are justified only when a large number of similar determinations are required, in which case they may be very convenient.

The use of "hybrid" expressions, such as "milligrams of zinc per square inch," "grams of glue per gallon," etc., is entirely unjustified. It is just as easy for a plater to obtain a conception of the magnitude of a square centimeter as of a milligram; and any use of hybrid units by chemists is a reflection upon the intelligence of the plater, or an indication of mental laziness of the chemist.

In Table 6 in the Appendix will be found a number of simple conversion factors, by means of which results obtained in the metric system can be expressed in the ordinary units and vice versa. It will be noted that to convert the concentration (in grams per liter) to *percentage by weight*, we divide the concen-

[1] HALL, E. J., *Metal Industry*, vol. 12, p. 466, 1914. The "assay gallon" for troy oz./gal. is 12.2 c.c.

tration in grams per liter by 10 times the specific gravity of the solution (or, more strictly speaking, the density of the solution, *i.e.*, the weight in grams of 1 c.c.). In this connection it is in place to call attention to the uncertainty that frequently arises through expressing concentrations in percentage. If a solution is stated to contain 20 per cent of copper sulphate, such an expression if correctly used means that the solution contains in each 100 g. or 100 lb. *of solution*, 20 g. or lb. respectively of copper sulphate, and 80 g. or lb. of water. Even when the expression is used correctly, it is of little value to an electroplater, who rarely if ever weighs the water or the solutions used by him. The term "per cent" is often used incorrectly, even by persons engaged in scientific work, who sometimes state that a solution contains 20 per cent of copper sulphate when it has been prepared by dissolving 20 g. of copper sulphate in 100 c.c. of water, or else in sufficient water to make 100 c.c. of solution. To avoid any confusion, it is preferable to eliminate the expression "per cent" as applied to such solutions, and in all cases to express the concentration in terms of the weight of substance present in a definite volume of solution, either in grams per liter or in ounces per gallon. In making use of such values the plater should bear in mind that in order to prepare 100 gal. of a solution to contain 20 oz. per gallon of copper sulphate, the necessary amount of copper sulphate (*i.e.*, 2,000 oz. or 125 lb.) should not be dissolved in 100 gal. of water (which would produce slightly over 100 gal. of solution), but in sufficient water to make 100 gal. of solution. In other words, the copper sulphate should be dissolved in a volume of water slightly less than that required, and the solution should be finally diluted with water to a volume of 100 gal., as indicated by some convenient mark on the tank. It is important to remember that the British imperial gallon is about 20 per cent larger than the U. S. gallon.

For research and investigation work, it will usually be found preferable to express the concentrations in terms of "normality" (see page 27), *i.e.*, in terms of the chemical equivalents of the various substances present in the solution. Through failure to calculate the relative normalities of solutions used in investigations, erroneous conclusions may be drawn or important deductions may be overlooked. When, however, such researches lead to the recommendation of certain solutions in commercial work, it is necessary that the concentrations should be expressed in grams per liter or ounces per gallon.

CHAPTER III

PRINCIPLES OF CHEMISTRY

It is obviously impossible in a brief chapter of a book of this scope even to touch upon all the principles of chemistry which electroplaters may consciously or unconsciously apply in their industry. For such information, chemical texts should be consulted, and if possible classes should be attended. Nevertheless, it is desirable to explain briefly the most important principles and terms likely to be employed. In doing so, the needs of electroplaters will be especially considered even though thereby the definitions or illustrations may be more restricted than would be otherwise desirable.

1. MATTER

Kinds of Matter.—*Matter* may be defined as that which has weight (or mass) and occupies space. A *substance* is any specific kind of matter, such as wood, lead, water, sodium carbonate, etc. Substances are distinguished from each other, and are hence identified, by their *properties*, such as color, taste, odor, specific gravity, solubility (in water or other solvents), melting point, boiling point, electrical conductivity, etc. Whenever two samples have identical properties, the samples are of the identical substance. Actually, it is usually necessary to observe or determine only a few properties in order to identify a substance, although obviously the more properties are determined the more reliable is the identification.

Of those substances which are homogeneous, *i.e.*, uniform in composition throughout, we distinguish two classes, known respectively as *elements* and *compounds*.

Elements may for convenience be defined as substances which have never been decomposed or separated into simpler substances by chemical methods. (The discovery of radium and the study of radioactive changes have shown that under certain circumstances some of the so-called elements may decompose, although such decomposition cannot at present be controlled by human

agencies.) Familiar examples of elements are oxygen and nitrogen, the gases which constitute the larger part of the atmosphere; carbon, sulphur, and phosphorus, all of which are non-metallic; and the metallic elements, such as copper, silver, gold, lead, tin, zinc, etc.

Compounds are substances which are uniform in composition throughout and which contain two or more elements, which elements are always present in a definite and constant proportion by weight. Thus, for example, water is a compound which consists always of 88.9 per cent (by weight) of oxygen, and 11.1 per cent of hydrogen. Similarly, sulphuric acid consists of hydrogen, sulphur, and oxygen, in definite proportions by weight. Invariably plating solutions contain one or more compounds in addition to water.

Mixtures may be distinguished from compounds by the fact that they consist of two or more substances (which may be either elements or compounds) which are present in many variable proportions, and which retain their original properties in the mixture. The classical example of a mixture, given in many chemistry texts, is that produced by grinding together sulphur and iron filings. From such a mixture the iron can still be removed by a magnet, and the sulphur by a suitable solvent for sulphur, such as carbon disulphide, showing that each substance has retained its original properties. If, however, such a mixture is heated, a chemical change or reaction occurs and a chemical compound, iron sulphide, is formed, which has neither the properties of iron nor of sulphur. Similarly, it is well known that the compound called "copper sulphate" has entirely different properties, such as color, density, solubility, taste, etc., than has a mere mixture of copper, sulphur, oxygen, and water, all of which substances are present in definite proportions in the blue crystals of copper sulphate.

As is usually the case in attempts to classify nature, there is no sharp line of demarcation between compounds and mixtures. Some classes of substances, especially solutions and alloys, are on the border line, so that from one standpoint they may be considered as compounds, and from another as mixtures. Certain properties of solutions will be discussed in detail (page 22), as solutions are the basis of all electroplating operations.

Structure of Matter.—The various elements are considered to be made up of small particles called *atoms*. An atom of an

element may conveniently be described as the smallest particle of that element that can enter into chemical combination. (Modern theories of chemistry and physics indicate that atoms are in turn composed of much smaller particles, or *electrons*, which need not, however, be considered in a book of this scope.) When a chemical compound is formed we consider that a simple number of atoms of one element combine with a simple number of atoms of one or more other elements, to form molecules of the compounds. A *molecule* of a compound is the smallest particle of that compound that can exist and retain the properties of the compound. Thus we consider that a molecule of water (represented as H_2O) is formed by the union of two atoms of hydrogen and one of oxygen. Elements may also exist in the form of molecules, which usually consist of two or more atoms. Thus a molecule of hydrogen is represented by H_2.

2. CHANGES IN MATTER

Physical Changes.—Temporary changes in matter, such as a change in temperature, or a change in physical state (as produced by melting or boiling), are known as *physical* changes.

Chemical Changes.—Permanent changes which occur in matter are known as *chemical* changes. Typical examples of chemical changes are as follows: (*a*) The *combination* of elements to form compounds, as when iron combines with the oxygen of the air to form rust, or iron oxide, which is a compound of iron and oxygen. (*b*) The *decomposition* of compounds into elements or into simpler compounds. Thus, when a compound known as "mercuric oxide" is heated, it is readily decomposed into mercury (or quicksilver) and oxygen. A less simple decomposition occurs in every electroplating operation. Thus, when a direct current is passed through a solution containing copper sulphate, the latter is decomposed into copper (which deposits upon the cathode) and a residue (or radical) containing sulphur and oxygen (which residue recombines with the anode, if the latter is copper, and forms copper sulphate). (*c*) *Double decomposition*, in which two compounds react with each other to form two different compounds. Thus, when sodium chloride is added to a solution of silver nitrate (such as is formed by dissolving silver in nitric acid), a white insoluble precipitate of silver chloride is formed, and there is also produced in the solution a soluble compound, sodium nitrate. Similarly, whenever an acid such

as sulphuric acid is neutralized with a base or alkali, such as sodium hydroxide (caustic soda), a new compound (in this case sodium sulphate) and water are formed by double decomposition.

Conservation of Matter.—Whenever the above chemical changes take place the total weight or mass of all the products of the change or *reaction* is exactly equal to the weight of all the substances entering into the reaction. The law of conservation of matter states that matter can neither be created nor destroyed.

3. ENERGY

Forms of Energy.—All chemical changes are accompanied by some change in the form of *energy*. The various forms of energy, such as heat, light, electricity, magnetism, chemical energy, and mechanical energy, can under appropriate conditions be converted into each other; and just as with matter, the total amount of energy remains unchanged. Thus, for example, coal contains a certain amount of chemical energy (derived originally from the energy of the sun). When coal burns (*i.e.*, combines with the oxygen of the air), this chemical energy is converted into heat, which through the expansion of steam in a steam engine may be changed into mechanical energy. The engine may in turn be connected to a generator and thereby produce electrical energy, which can be reconverted to mechanical energy in an electric motor. Or the electrical energy can be applied to a storage cell, in which it is converted into chemical energy, *i.e.*, it produces new substances in the storage cell which, by reacting with each other, can again produce electricity. When a current of electricity is passed through a plating solution, most of the energy is converted into heat, though part may be used in decomposing the chemical compounds present. (In the ideal case, with anode and cathode of identical composition and physical properties, with no polarization, and with perfect anode and cathode efficiency, all the electrical energy is converted into heat.) A consideration of these relations between energy and chemical changes is essential to any understanding of electroplating operations.

4. CHEMICAL NOTATION

For convenience in writing and in calculations, there is assigned to each element an abbreviation or symbol, and a number, known as its *atomic weight*. This number represents the proportion in

which, or in some simple multiple of which, that element always enters into chemical combination. (See Table 7, Appendix.) These numbers are only relative, and are at present based upon the atomic weight of oxygen as 16, although originally based upon hydrogen, the lightest of the elements, as 1. (Considering oxygen as 16, the atomic weight of hydrogen is 1.008, but for most practical purposes we may consider it as 1.) By the appropriate arrangement of the symbols of the elements it is possible to indicate very concisely the formula or composition of any chemical compound; and by the combination of such formulas into *equations*, the changes which take place in any reaction can be represented. It should be borne in mind that the use of symbols, formulas, and equations is simply a sort of chemical shorthand, and, just as in shorthand, the symbols have no significance except insofar as they represent facts. There is no magic in chemical formulas or equations and there is absolutely no justification for using them unless the underlying facts are understood, and then only as a brief, explicit method of stating such facts.

If, as an illustration, we say that the chemical formula of water is H_2O, this formula states very explicitly certain facts, *viz.*, that water always consists of hydrogen and oxygen in the proportion of two atoms of hydrogen to one atom of oxygen, or of 2 parts by weight of hydrogen to 16 parts by weight of oxygen in each 18 parts (*i.e.*, the *molecular weight*) of water. Every 18 g. or lb. of water contains, therefore, 2 g. or lb. respectively of hydrogen, and 16 g. or lb. of oxygen; or in other words, 1/9, or 11.1 per cent, of hydrogen, and 8/9, or 88.9 per cent, of oxygen.

5. CHEMICAL CALCULATIONS

The use of formulas to represent chemical compounds, and of equations to represent chemical changes, is the basis of all chemical calculations. As the name implies, an equation is correct only if the quantity (*i.e.*, number of atoms) of each element is the same on each side of the equation. But even such an equality is not evidence of the chemical correctness of the equation. Before an equation can be written it is necessary to know what reaction, if any, occurs between the substances used, and what substances are produced as a result of such a reaction. Thus, if it has been found experimentally that when sodium cyanide (NaCN) is added to a solution of silver nitrate ($AgNO_3$) there are formed

a white precipitate of silver cyanide (AgCN) and a solution of a salt, sodium nitrate ($NaNO_3$), these facts can be represented by an equation such as the following:

Sodium cyanide + Silver nitrate = Silver cyanide + Sodium nitrate

$$NaCN + AgNO_3 = AgCN + NaNO_3$$

If in this equation we introduce the atomic weights of the respective elements, we obtain the molecular weights of the various compounds:

$$\underset{23+12+14}{NaCN} + \underset{108+14+(3\times 16)}{AgNO_3} = \underset{108+12+14}{AgCN} + \underset{23+14+(3\times 16)}{NaNO_3}$$

$$\underset{49}{} \qquad \underset{170}{} \qquad \underset{134}{} \qquad \underset{85}{}$$

In other words, 49 parts by weight (*e.g.*, grams or pounds) of sodium cyanide are required to react with 170 parts of silver nitrate, and there are formed 134 parts of silver cyanide and 85 parts of sodium nitrate. These substances react with each other always in *these proportions by weight.* With such information, it is possible to determine by simple calculations just how much of each substance will be required to react with a given amount of another substance or to produce a desired amount of some other substance.

Example.—Thus, in the above illustration, suppose it is desired to know how much sodium cyanide is necessary to precipitate the silver from 100 oz. of silver nitrate, to form silver cyanide, such as might be desired to prepare a cyanide silver plating solution. Since, according to the above equation, 49 oz. of sodium cyanide are needed for 170 oz. of silver nitrate, it requires $\frac{49}{170}$ oz. of sodium cyanide for each ounce of silver nitrate, and therefore for 100 oz. of silver nitrate $\frac{49}{170} \times 100 = \frac{4,900}{170} = 28.7$ oz. of sodium cyanide are required. Or again, suppose we wish to know how much silver cyanide can be prepared from 100 oz. of silver nitrate. Since 170 oz. of silver nitrate yield 134 oz. of silver cyanide, 100 ounces of silver nitrate will produce $\frac{134}{170} \times 100 = \frac{13,400}{170} = 79$ oz. of silver cyanide.

In short, all that is necessary to solve such problems is to determine from the equation in what proportion by weight the substances in question enter into the reaction and then to determine the unknown or desired quantity by the use of this same proportion.

As a precaution against confusion in such calculations, always check the result by "common sense" methods. Thus, in the

first of the above problems, simple inspection of the equation shows that 170 parts of silver nitrate require 49 parts of sodium cyanide, or slightly less than one-third of the weight of silver nitrate; hence it is evident that the result, 28.7 oz. of sodium cyanide for 100 oz. of silver nitrate, is at least approximately correct. If, on the other hand, the proportion had been accidentally reversed, and written $\frac{170}{49}$, the result obtained for 100 oz. of silver nitrate would have been 347 oz. of sodium cyanide, which is obviously incorrect. Similarly, in the second problem it is evident that the weight of silver cyanide must be somewhat less than that of the silver nitrate from which it is produced.

Example.—As a further illustration of the use of such an equation let us solve the following problem. It is desired to prepare 100 gal. of a silver plating solution to contain 3 oz./gal. of silver cyanide. (*a*) How much metallic silver must be dissolved in nitric acid to form a solution from which the required amount of silver cyanide can be precipitated; and (*b*) how much sodium cyanide must be used in the precipitation? (*a*) 100 gal. of solution will require 300 oz. of silver cyanide. From the equation we note that 170 parts of silver nitrate (containing 108 parts of silver) are required to form 134 parts of silver cyanide; in other words, 108 parts of silver form 134 parts of silver cyanide. Therefore each ounce of silver cyanide will require $\frac{108}{134}$ oz. of silver,[1] and 300 oz. of silver cyanide will require $\frac{108}{134} \times 300 = \frac{32{,}400}{134} = 242$ oz. of metallic silver. (*b*) Since to precipitate 134 parts of silver cyanide requires 49 parts of sodium cyanide, each ounce of silver cyanide will require $\frac{49}{134}$ oz. of sodium cyanide, or 300 oz. of silver cyanide will require for its precipitation $\frac{49}{134} \times 300 = \frac{14{,}700}{134} = 111$ oz. of sodium cyanide.[2]

Confidence in such calculations can be gained only by practice. Platers are therefore urged to make such calculations frequently, in each case making sure from appropriate texts that the problems are based on correct equations.

6. CLASSES OF CHEMICAL COMPOUNDS

In the study of chemistry it is convenient to make a distinction between organic and inorganic compounds. The original basis

[1] For simplicity all these calculations are made in avoirdupois ounces. Actually the silver would be purchased in troy ounces (see Table 5).

[2] It will require an equal amount of sodium cyanide to redissolve the silver cyanide.

for such a distinction was the occurrence of the organic compounds in living organisms, *i.e.*, in animal and vegetable life. That distinction ceased to exist, however, when it was found possible to produce by artificial means many of such "organic" compounds. The present distinction is therefore an artificial one, and we may define *organic chemistry* as the chemistry of the compounds of carbon, and *inorganic chemistry* as that of all other compounds. (For arbitrary reasons carbon itself, the oxides of carbon, and carbonic acid and carbonates are usually included in inorganic chemistry.) There are a great many classes of organic compounds, such as hydrocarbons, alcohols, organic acids, carbohydrates, etc. Many such compounds are used directly or indirectly in electroplating and electroforming, such as alcohol, benzene, glue, etc. Since, however, they only rarely enter into the actual composition of plating solutions, and then usually in very small amounts, it will not be necessary to discuss them further, except as they may be incidentally referred to.

By far the greater number of compounds entering into plating solutions are inorganic. The simplest inorganic compounds are the *binary* compounds, *i.e.*, those which consist only of two elements. In general, binary compounds are designated by names ending in *ide*, as oxide, sulphide, chloride, etc., preceded by the name of the other element, usually the more metallic of the two. Thus, iron sulphide is a compound of iron and sulphur, sodium chloride, one of sodium and chlorine, etc. Although the names of such compounds usually indicate what elements are present in them, it is not possible to write formulas for such compounds without a knowledge of the relative proportions in which these particular elements combine—in other words, their valence.

Valence.—By the *valence* of an element is meant the number of atoms of hydrogen with which one atom of the element will combine, or which it will replace. Thus in water (H_2O) one atom of oxygen combines with two atoms of hydrogen; therefore the valence of oxygen is two. Similarly, in hydrochloric acid (HCl) one atom of chlorine combines with one of hydrogen, and therefore in this compound the valence of chlorine is one. In ammonia (NH_3) one atom of nitrogen combines with three of hydrogen; hence in this compound the valence of nitrogen is three. Some of the elements, especially the metals, do not readily

combine with hydrogen, but under proper conditions they may replace hydrogen. Thus it is possible to replace one atom of hydrogen in hydrochloric acid (HCl) by one atom of sodium (Na) to form sodium chloride (NaCl); hence the valence of sodium is one. In sulphuric acid (H_2SO_4) it therefore requires two sodium atoms to replace the two hydrogen atoms, forming sodium sulphate (Na_2SO_4). If, however, instead of sodium, the metal calcium (or a suitable compound of calcium) is employed, it will be found that calcium sulphate ($CaSO_4$) is formed, in which one atom of calcium has replaced two atoms of hydrogen; in other words, the valence of calcium is two. Many of the elements exhibit several valences, according to the type of compound in which they are present. In each type of compound, however, the valence of the element remains the same. Thus iron has two principal valences, which are respectively two and three. All the compounds in which iron has a valence of two are designated as *ferrous* compounds, and those in which it has a valence of three are *ferric* compounds. Thus ferrous chloride is $FeCl_2$, *i.e.*, one atom of iron combines with two atoms of chlorine (each of which, as illustrated above, has a valence of one in hydrochloric acid and chlorides). Ferric chloride has the formula $FeCl_3$, *i.e*, one atom of iron combines with three of chlorine. Copper has a valence of one in cuprous compounds such as cuprous chloride (CuCl), and of two in cupric compounds such as cupric chloride ($CuCl_2$).

It is sometimes convenient to designate as positive (+) the valence of those elements which are either metallic, or which in a particular case are able to replace hydrogen or to combine with oxygen; and as negative (−) the valence of those elements which are able to combine with hydrogen or to replace oxygen. The valence of hydrogen is always considered as +I and that of oxygen as −II. (To avoid confusion, Roman numerals are used to indicate valence.) In every chemical compound the sum of the positive valences must always equal the sum of the negative valences, *i.e.*, the "algebraic sum" is always zero. Thus ferric chloride may be written $Fe^{+III}Cl_3^{-I}$, from which it may be seen that there are three positive valences and three negative valences. For convenience, we consider that a free element, such as carbon or sulphur or iron, existing as such, has a valence of zero. Therefore the valences assigned to the various elements apply only when those elements are present in compounds.

In Table 8 in the Appendix will be found a list of the valences of the common elements in their principal types of compounds. By the proper use of such tables the probable formulas of any binary compounds may be determined, by using the simplest number of atoms of each element which will make the total valence of each element equal and of opposite sign.

Problem.—What is the formula of calcium sulphide? Since from the table the valence of calcium is $^{+II}$, and that of sulphur *in sulphides* is $^{-II}$, one atom of calcium is equivalent to one of sulphur, and the formula of calcium sulphide is CaS or $Ca^{+II}S^{-II}$.

Problem.—What is the formula of sodium sulphide? Since the valence of sodium is $^{+I}$ and that of sulphur in sulphides is $^{-II}$, it will require two atoms of sodium to combine with one of sulphur, and therefore the formula of sodium sulphide is Na_2S (*i.e.*, $Na_2{}^{+I}S^{-II}$).

Problem.—What are the formulas of ferrous oxide and ferric oxide respectively? As the valence of iron in ferrous compounds is $^{+II}$, and that of oxygen is $^{-II}$, the formula of ferrous oxide is FeO. As the valence of iron in ferric compounds is $^{+III}$, and that of oxygen is $^{-II}$, the simplest way to combine the two elements is to use two atoms of iron (having a total valence of $^{+VI}$) and three atoms of oxygen (having a total valence of $^{-VI}$). The formula is therefore Fe_2O_3.

Oxidation and Reduction.—Whenever by means of a chemical reaction the valence of an element is increased (algebraically), the reaction is called an *oxidation*[1] (even though oxygen as such may not necessarily enter into the equation); and when the valence is decreased, *reduction* takes place. Thus if ferrous oxide (FeO) is changed to ferric oxide (Fe_2O_3), or if ferrous chloride ($FeCl_2$) is changed to ferric chloride ($FeCl_3$), in each case the iron has been *oxidized* from the ferrous to the ferric condition, *i.e.*, from a valence of $^{+II}$ to $^{+III}$. In all chemical reactions involving oxidation of one element, there must be a corresponding reduction of some other element; and the total increase of valence of the one element must be equal to the decrease of valence of the other element. That compound in which the valence of the element is increased is (in the particular reaction involved) a *reducing agent*; and that in which the valence is decreased is an *oxidizing agent*. As a simple example of oxidation and reduction (which must always occur simultaneously) we may take the action of stannous (tin) chloride ($SnCl_2$) upon ferric chloride ($FeCl_3$) to produce stannic chloride

[1] In a restricted sense the term "oxidation" is used to indicate the combination of a substance with oxygen.

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($SnCl_4$) and ferrous chloride ($FeCl_2$). This reaction is often employed in the determination of the amount of iron in a solution. The above reaction may be written as follows:

$$Sn^{+II}Cl_2 + 2Fe^{+III}Cl_3 = Sn^{+IV}Cl_4 + 2Fe^{+II}Cl_2$$

From the numbers above the symbols Sn and Fe, indicating their respective valences, it will be noted that each atom of tin has increased in valence from $^{+II}$ to $^{+IV}$, *i.e.*, it has been oxidized; while each atom of iron has decreased in valence from $^{+III}$ to $^{+II}$, or has been reduced. (For simplicity only the valences of those elements which are actually oxidized or reduced are introduced into the above equation.) In this reaction, therefore, the stannous chloride serves as a reducing agent, and the ferric chloride as an oxidizing agent. Most equations representing the reactions which occur during oxidation and reduction are much more complicated than the above example; but all are based on the same principles.

7. ELECTROLYTIC DISSOCIATION

Although a large variety of substances are soluble in water, it has been found that only certain aqueous solutions, *viz.*, those which contain acids, bases, or salts, will conduct electricity. From a study of other properties of these solutions, especially their boiling points and freezing points, we are led to the conclusion that when acids, bases, or salts are dissolved in water, they are broken up or dissociated, to a certain extent at least, into particles called *ions*, which consist of atoms or groups of atoms. These ions are electrically charged, regardless of whether a current is passed through the solution or not. When a current is passed through, the charged particles are carried by the current and discharged at the electrodes. The negatively charged particles or *anions* are carried to the positively charged pole or anode; and the positively charged particles or *cations* are carried to the negatively charged pole or cathode. By the discharge of the ions at the electrodes their charges are hence neutralized electrically.

If a substance such as hydrochloric acid (HCl) is dissolved in water, its dissociation may be represented as follows:

$$HCl \leftrightarrows H^+ + Cl^-$$

(In this form of expression the number of plus or minus signs is equal to the valence of the ion.) In other words, each of the

molecules of hydrochloric acid that dissociates forms a positively charged hydrogen ion and a negatively charged chloride ion. The double arrow indicates that this reaction (like all electrolytic dissociation) is reversible. If hydrochloric acid is dissolved in water a part is dissociated or the reaction goes from left to right, but if on the other hand, hydrogen ions and chloride ions are brought together in a solution a certain proportion of them will combine to form hydrochloric acid, *i.e.*, the reaction proceeds from right to left.

With a more complex substance, such as sulphuric acid (H_2SO_4), the dissociation occurs as follows:

$$H_2SO_4 \leftrightarrows 2H^+ + SO_4^{--}$$

Actually the dissociation occurs in two stages, represented as follows:

$$H_2SO_4 \leftrightarrows H^+ + HSO_4^-$$
$$HSO_4^- \leftrightarrows H^+ + SO_4^{--}$$

The products of the second dissociation are known as hydrogen ions and sulphate ions. More details of the theory of electrolytic dissociation may be found in the regular texts on general and physical chemistry. With a knowledge of these simple principles of electrolytic dissociation, the relation of acids, bases, and salts may be more clearly understood.

7. ACIDS, BASES, AND SALTS

Acids.—Acids are those substances which contain hydrogen, which hydrogen is replaceable by metals to form salts. Acids are also capable of neutralizing bases to form salts. When dissolved in water, acids are dissociated, to some extent at least, with the formation of hydrogen ions. Sulphuric acid (H_2SO_4) is a compound in which the two hydrogen atoms can be replaced by metals to form salts. When sulphuric acid acts upon zinc, a gas (hydrogen) is evolved and a salt (zinc sulphate) is formed in the solution. This may be shown by the equation:

$$Zn + H_2SO_4 = ZnSO_4 + H_2$$

from which it may be seen that the zinc has taken the place of the hydrogen.

When sulphuric acid is added to a base such as sodium hydroxide (NaOH), a reaction known as *neutralization* occurs, as a

result of which there are formed water and a salt, in this case sodium sulphate (Na_2SO_4), according to the following equation:

$$H_2SO_4 + 2NaOH = Na_2SO_4 + 2H_2O$$

The extent to which an acid is dissociated when dissolved in water, or in other words the proportion of hydrogen ions formed, is an indication of the strength or "acidity" of an acid. Thus, if in equivalent concentrations it is found that hydrochloric acid is dissociated to the extent of 95 per cent, and sulphuric acid only 90 per cent, the hydrochloric acid is a stronger acid than the sulphuric acid, considered *as an acid, i.e.*, with respect to its power to neutralize bases. (The corrosive actions of concentrated sulphuric acid or nitric acid upon organic matter, such as wood, etc., or of hydrofluoric acid upon glass, are specific properties, not necessarily connected with the acidity of the acids, and are not an indication of the *strength* of the acids.) Hydrochloric, sulphuric, and nitric acids are the three principal *strong* acids; while acetic and citric acids are fairly weak acids, and boric and carbonic acids are very weak.[1] The degree of the sour taste of acids is roughly proportional to their strength as measured by their hydrogen ion concentration.

In general, acids are formed from the non-metallic elements, such as chlorine, sulphur, nitrogen, phosphorus, etc. Binary acids, such as hydrochloric acid (HCl) and hydrosulphuric acid or hydrogen sulphide (H_2S), may be considered as compounds of the element directly with hydrogen. The acids containing oxygen, such as sulphuric acid (H_2SO_4), nitric acid (HNO_3), phosphoric acid (H_3PO_4), and carbonic acid (H_2CO_3), may be conveniently considered as produced by the combination of water with the appropriate non-metallic oxides, which oxides are then known as the *anhydrides* of the acids. Thus we may consider that:

Sulphur trioxide, $SO_3 + H_2O = H_2SO_4$, sulphuric acid.
Nitrogen pentoxide, $N_2O_5 + H_2O = 2HNO_3$, nitric acid.
Phosphorus pentoxide, $P_2O_5 + 3H_2O = 2H_3PO_4$, phosphoric acid.
Carbon dioxide, $CO_2 + H_2O = H_2CO_3$, carbonic acid.

[1] The strong acids are often called *mineral* acids. This usage, in so far as it implies a distinction from *organic* acids, is inappropriate, as many inorganic acids are weaker than certain organic acids.

Acids such as hydrochloric acid (HCl) and nitric acid (HNO_3), which contain only one replaceable atom of hydrogen in each molecule, are *monobasic;* those, such as sulphuric acid (H_2SO_4), with two replaceable hydrogen atoms, are *dibasic;* and with three replaceable hydrogen atoms, as phosphoric acid (H_3PO_4), are *tribasic.*

Bases.—Bases are hydroxides of metallic elements, *i.e.,* compounds of a metal with hydrogen and oxygen, such as sodium hydroxide or caustic soda (NaOH), calcium hydroxide or hydrated lime, $Ca(OH)_2$, etc. In general, they have the power to combine with acids to form salts and water. They may be considered as made up of the oxide of a metal and water, thus:

Sodium oxide, $Na_2O + H_2O = 2NaOH$, sodium hydroxide.
Calcium oxide (lime), $CaO + H_2O = Ca(OH)_2$, calcium hydroxide.

When dissolved in water they usually have an "alkaline" taste and a soapy feeling. Those bases such as sodium hydroxide (NaOH) and potassium hydroxide (KOH) which are readily soluble in water are called *alkalis.* Ammonium hydroxide (NH_4OH), ordinary aqua ammonia, which is produced by dissolving ammonia gas (NH_3) in water, is also usually classed with the alkalis, since it has basic properties similar to them.

When a base is dissolved in water, it is dissociated, to some degree at least, with the formation of hydroxyl ions (OH^-), and the extent to which such dissociation occurs is a measure of the strength of the base. Thus sodium and potassium hydroxides are strong bases because in solution they are largely dissociated, while ammonium hydroxide is less dissociated and is hence a weaker base. (Owing to the very slight solubility of most of the metallic hydroxides, it is difficult to determine directly their relative strength as bases.) The dissociation of a strong base may be represented as follows:

$$NaOH \rightleftharpoons Na^+ + OH^-$$

Salts.—Salts may be considered as derived from acids, either through the replacement of the hydrogen of the acid by a metal, or through the neutralization of the acid by a base. If the former reaction takes place directly, hydrogen is given off, thus:

$$Zn + H_2SO_4 = ZnSO_4 + H_2$$

In the latter case, *i.e.*, whenever neutralization of an acid by a base occurs, water is always formed in addition to a salt, thus:

$$Zn(OH)_2(\text{zinc hydroxide}) + H_2SO_4 = ZnSO_4(\text{zinc sulphate}) + 2H_2O$$

$$2NaOH(\text{sodium hydroxide}) + H_2SO_4 = Na_2SO_4(\text{sodium sulphate}) + 2H_2O$$

The *names* of salts contain, in addition to the name of the metal, a term derived from the name of the corresponding acid according to the following simple rules:

Salts containing only two elements, *i.e.*, derived from acids containing only two elements, always end in *ide;* thus all salts of hydrochloric acid (HCl) are *chlorides.*

Salts of acids which contain oxygen and whose names end in *ic,* always end in *ate;* thus salts of chloric acid ($HClO_3$) are chlorates, of nitric acid (HNO_3) are nitrates, of carbonic acid (H_2CO_3) are carbonates, etc.

Salts of acids which contain oxygen, and whose names end in *ous,* always end in *ite;* thus salts of chlorous acid ($HClO_2$) are chlorites, of nitrous acid (HNO_2) are nitrites, etc.

These principles can be illustrated by the following list of acids of sulphur and their corresponding sodium salts:

Acid		Salt	
Hydrosulphuric[1]	H_2S	Sodium sulphide	Na_2S
Hyposulphurous	H_2SO_2	Sodium hyposulphite[2]	Na_2SO_2
Sulphurous	H_2SO_3	Sodium sulphite	Na_2SO_3
Sulphuric	H_2SO_4	Sodium sulphate	Na_2SO_4
Persulphuric	$H_2S_2O_8$	Sodium persulphate	$Na_2S_2O_8$

[1] More commonly named "hydrogen sulphide."

[2] The salt usually called "hyposulphite" of soda, or "hypo," is erroneously designated. Its formula is $Na_2S_2O_3$ and its correct name is sodium thiosulphate.

The *formula* of a salt derived from a given acid and metal may be determined from the principles of valence discussed on page 19. If the formula of the acid and the valence of the metal are known, all that is necessary is to replace the hydrogen in the acid by the appropriate number of atoms of the metal.

Problem.—What are the name and formula of the potassium salt of hydrochloric acid? Since hydrochloric acid contains only two elements, its salts are chlor*ides.* The formula of hydrochloric acid is HCl, and the valence of potassium (K) is $^{+I}$; therefore one atom of potassium will replace one of hydrogen, to form KCl, or potassium chloride.

Problem.—What are the name and formula of the calcium salt of nitric acid? The formula of nitric acid is HNO_3, *i.e.*, it contains oxygen and the name ends in *ic;* therefore its salts are nitrates. The valence of calcium is $^{+II}$. In order to secure the two atoms of hydrogen to be replaced with one atom of calcium, it is necessary to use two molecules of nitric acid. The formula of the salt is therefore $Ca(NO_3)_2$, or calcium nitrate.

When salts are dissolved in water they are dissociated to some extent, with the formation of *cations* (positively charged ions), containing the metal of the salts, and *anions* (negatively charged *ions*), containing the acid group present in the salt, in accordance with such equations as the following:

$$NaCl \leftrightarrows Na^+ + Cl^-$$
$$Na_2SO_4 \leftrightarrows 2Na^+ + SO_4^{--}$$
$$CuSO_4 \leftrightarrows Cu^{++} + SO_4^{--}$$

Normal Solutions.—From a consideration of the following equations it may be noted that one molecule of hydrochloric acid will combine with one molecule of sodium hydroxide (in which the valence of sodium is one); and that it requires two molecules of hydrochloric acid for one molecule of cupric hydroxide (in which the valence of copper is two). On the other hand, one molecule of sulphuric acid combines with two of sodium hydroxide, and with one of cupric hydroxide.

$$\begin{array}{rcl} HCl + NaOH & = & NaCl + H_2O \\ 36.5 \quad 40 & & \\ 2HCl + Cu(OH)_2 & = & CuCl_2 + 2H_2O \\ 73 \quad 98 & & \\ H_2SO_4 + 2NaOH & = & Na_2SO_4 + 2H_2O \\ 98 \quad 80 & & \\ H_2SO_4 + Cu(OH)_2 & = & CuSO_4 + 2H_2O \\ 98 \quad 98 & & \end{array}$$

It is evident that a liter of sulphuric acid containing a weight in grams of sulphuric acid equal to the molecular weight of the sulphuric acid, *i.e.*, 98 g., would neutralize twice as much sodium hydroxide as would a liter of hydrochloric acid containing the molecular weight in grams of hydrochloric acid (*i.e.*, 36.5 g.). In order, therefore, to obtain a solution of sulphuric acid which would be equivalent to that of hydrochloric acid containing 36.5 g. per liter, we would require not 98, but one-half that amount, or 49 g. of sulphuric acid per liter. Such a solution of

sulphuric acid is a *normal solution.* A normal solution of any substance is a solution containing in each liter a weight in grams equal to the equivalent weight of that substance. The equivalent weight of an acid is the weight of the acid equivalent to one atom of replaceable hydrogen, or, in other words, the molecular weight of the acid divided by the number of replaceable hydrogen atoms. Therefore a normal solution of hydrochloric acid (HCl) contains 36.5 g. per liter; of sulphuric acid (H_2SO_4), $\frac{98}{2} = 49$ g. per liter; of phosphoric acid (H_3PO_4), $\frac{98}{3} = 32.7$ g. per liter. Similarly, the equivalent weight of a base is equal to its molecular weight divided by the number of replaceable hydroxyl groups. Therefore a normal solution of sodium hydroxide (NaOH) contains 40 g. per liter; and of calcium hydroxide, $Ca(OH)_2$, $\frac{74}{2} = 37$ g. per liter. The equivalent weight of a salt is the molecular weight divided by the valence of either the total metal or acid groups in it. Thus a normal solution of sodium chloride (NaCl) will contain 58.5 g. per liter; of sodium sulphate (Na_2SO_4), $\frac{142}{2} = 71$ g. per liter; and of anhydrous copper sulphate ($CuSO_4$), $\frac{160}{2} = 80$ g. per liter. With respect to oxidation or reduction, the equivalent weight of a compound is equal to the molecular weight divided by the number of valences which it gains or loses in the reaction.

From these definitions it follows that equal volumes of all normal solutions are chemically equivalent to each other. Thus 100 c.c. of normal sodium hydroxide solution will exactly neutralize 100 c.c. of normal sulphuric acid, or of any other normal acid. Solutions, instead of being always made normal (N), may have any definite fractional normality, thus half normal $\left(0.5\ N \text{ or } \frac{N}{2}\right)$, tenth normal $\left(0.1\ N \text{ or } \frac{N}{10}\right)$, etc., which indicates that they contain in each liter the corresponding fractional part of the equivalent weight.

Molar solutions are those which contain in 1 liter, one "gram molecule" or one "mol" of the substance, *i.e.*, a weight in grams equal to the molecular weight of the substance. Thus a molar

solution of sulphuric acid contains 98 g./1. of H_2SO_4, or twice as much as a normal solution. Molar solutions are most commonly referred to when dealing with substances that are not dissociated, such as dextrose, $C_6H_{12}O_6$, of which a molar solution (M) contains 180 g./1. The term molar is also frequently applied to chromic acid (p. 309) because for it the term normal may have two meanings.

Acid Salts.—When an acid molecule is dibasic, *i.e.*, contains two replaceable hydrogen atoms, it is possible to replace only one of the hydrogen atoms with a metal, forming an *acid* salt, *i.e.*, one which possesses some of the properties of an acid and some of a salt. Thus, if to a given amount of sulphuric acid there is added just half the amount of sodium hydroxide which would be required to neutralize the acid completely, the following reaction takes place:

$$H_2SO_4 + NaOH = NaHSO_4 + H_2O$$

The compound $NaHSO_4$ is an acid salt, known as sodium acid sulphate, sodium hydrogen sulphate, or sodium bisulphate (or commercially as niter cake, because it is formed as a by-product in the manufacture of nitric acid by the action of sulphuric acid upon sodium nitrate). That it still possesses acid properties is shown by its extensive use as a substitute for sulphuric acid in pickling. That it is not as strong as the original sulphuric acid is evident from the fact that when using it for pickling, it is necessary to use higher temperatures and longer periods than with sulphuric acid.

Basic Salts.—Similarly compounds are sometimes formed in which only part of the hydroxyl (OH) groups in the base are replaced by the acid groups or radicals. Such compounds are designated as *basic* salts. Thus aluminum hydroxide is $Al(OH)_3$, and if all the hydroxyl (OH) groups are replaced with Cl (by reaction with hydrochloric acid), aluminum chloride ($AlCl_3$) is produced. If, however, only one of the hydroxyl groups is replaced, we obtain $Al(OH)_2Cl$, which is basic aluminum chloride. When nickel plating solutions which contain iron become very nearly neutral, yellow basic compounds of iron usually separate. Such a compound as basic ferric sulphate might have the formula $Fe^{+I}(OH)SO_4$, although such compounds are usually more complicated in composition.

Indicators.—In describing the properties of acids and bases, attention might have been called to the fact that they produced

characteristic changes in the colors of certain organic dyes, which are therefore known as *indicators*. These substances can, however, best be considered with respect to the processes of neutralization and the formation and behavior of salts. For special purposes a great variety of indicators may be employed, but it will be sufficient at this time to consider three of the most common, namely, litmus, methyl orange, and phenolphthalein, the colors of which are as follows:

	Acid	Neutral	Alkaline
Litmus	Red	Purple	Blue
Methyl orange	Red	Orange	Yellow
Phenolphthalein	Colorless	Colorless	Pink

Formerly the most common application of indicators was in the neutralization of acids or bases, for the purpose of determining the amount of acid or base in a given sample of solution. (Now they are extensively used for measuring pH, see p. 101.) In the former operation, known as a *titration*, a measured amount, *e.g.*, 25 c.c., of the solution to be tested is placed in a small flask or beaker, and a very small amount of the indicator is added. If the sample contains free acid, an alkaline solution (*e.g.*, sodium hydroxide) of predetermined strength or concentration is run in from a burette or measuring tube until the indicator just changes color to the neutral tint. From the amount and concentration of the alkali added, the amount of acid present in the solution may be calculated. Suppose, that 25 c.c. of a sulphuric acid pickle required 30 c.c. of a normal sodium hydroxide solution (1 c.c. of which is equal to 0.049 g. of sulphuric acid). Then the 25-c.c. sample titrated must contain $0.049 \times 30 = 1.47$ g. of sulphuric acid; and therefore 1 liter (or 1,000 c.c.) will contain $1.47 \times \frac{1,000}{25} = 1.47 \times 40 = 58.8$ g. of sulphuric acid. Its strength is therefore 58.8 g./l., or 7.88 oz./gal., of sulphuric acid. The normality of the acid can be more conveniently calculated. If 25 c.c. of acid required 30 c.c. of normal alkali, the acid must be $\frac{30}{25} = 1.2N$.

When relatively strong acids, such as sulphuric, nitric, and hydrochloric, are to be titrated with strong bases, such as sodium or potassium hydroxide, it is practically immaterial as to which of the above indicators is employed, since any of them will give a sufficiently sharp color change or "end point." When, however, a weak acid, such as acetic acid, or a weak base, such as

ammonia, is to be titrated, it is necessary to choose the indicator which will give reliable results. Failure to do so may yield very erroneous results because of the hydrolysis of salts of weak acids or weak bases.

Hydrolysis.—In the previous discussion it was pointed out that as the result of the electrolytic dissociation of acids, hydrogen ions are formed, and of bases, hydroxyl ions, and also that whenever an acid is neutralized by a base, water is formed. The processes of dissociation and neutralization may therefore be represented as follows:

$$NaOH \leftrightharpoons Na^+ + OH^-$$

$$HCl \leftrightharpoons H^+ + Cl^-$$

$$NaOH + HCl \leftrightharpoons NaCl + H_2O$$

or $$(Na^+ + OH^-) + (H^+ + Cl^-) \leftrightharpoons Na^+ + Cl^- + H_2O$$

Since in the last form the Na^+ and Cl^- ions are present on both sides of the equation, we may consider that the only change that has taken place as a result of neutralization is that hydrogen ions of the acid have combined with hydroxyl ions of the base to form water, a substance which is practically undissociated. With strong bases and acids, *i.e.*, those which are highly dissociated and whose salts are highly dissociated, the principal reaction that occurs during neutralization is therefore

$$H^+ + OH^- \leftrightharpoons H_2O$$

As compared with strong acids or bases, water is practically undissociated. Actually, however, it has been found that pure water is dissociated to a very slight extent, that is, it contains a very small number of both hydrogen and hydroxyl ions. In pure (therefore neutral) water at 25°C. (77°F.) the concentration of hydrogen and hydroxyl ions is each equal to about $\frac{1}{10{,}000{,}000}$ normal, usually written $10^{-7}N$. At any given temperature in water, and in all aqueous solutions, the *product* of the hydrogen and hydroxyl ion concentrations is always the same; thus at 25°C. it is $10^{-14}\left(\text{or, } \frac{1}{10{,}000{,}000} \times \frac{1}{10{,}000{,}000}\right)$. This value of 10^{-14} is the *dissociation constant* of water at 25°C. It therefore follows that if to pure water an acid containing hydrogen ions is added, the hydrogen ion concentration is increased and the hydroxyl ion concentration correspondingly

decreased, but both kinds of ions are always present in some amount. Thus in a 0.01 N solution of hydrochloric acid we may assume that the hydrogen ion concentration $[H^+]$ is also 0.01 N, or, $10^{-2}N$; and therefore the hydroxyl ion concentration $[OH^-]$ must be $\frac{10^{-14}}{10^{-2}} = 10^{-12}N$.

Certain salts, such as sodium carbonate (Na_2CO_3), when dissolved in water have an alkaline reaction, which is evidence that the solution contains an excess of hydroxyl ions. In the above equations for neutralization the reversible sign was used, indicating that a salt may be decomposed, to a very slight extent at least, by the action of water. Such decomposition, which is known as *hydrolysis*, does not occur to any appreciable extent if the base and acid are both strong, since they would, if liberated, readily form hydrogen and hydroxyl ions which would recombine and form water. However, with a salt, such as sodium carbonate, derived from a weak acid (carbonic acid), there are not as many hydrogen ions produced by hydrolysis from the carbonic acid as there are hydroxyl ions from the sodium hydroxide. Consequently, the solution of the salt contains an excess of hydroxyl ions; in other words, it is alkaline to indicators, slightly so to phenolphthalein, and greatly so to litmus or methyl orange.

Similarly, certain salts, such as ammonium chloride (NH_4Cl), formed from ammonium hydroxide, a weak base, and hydrochloric acid, a strong acid, have an acid reaction. This also is the result of hydrolysis and is an evidence that there are more hydrogen ions produced from the small amount of hydrochloric acid set free than there are hydroxyl ions from the (necessarily) equivalent amount of ammonium hydroxide. Most of the hydroxides of the "heavy metals," such as copper, zinc, tin, lead, iron, nickel, etc., are weak bases; consequently their salts are slightly hydrolyzed with the formation of free acid. Hence we find that solutions of such salts as copper sulphate, zinc sulphate, tin chloride (stannous or stannic), lead fluoborate, ferric chloride, and nickel sulphate, all have an acid reaction when tested with an indicator such as litmus, the color of which changes at approximately 10^{-7}, the true neutral point. This fact has an important bearing on the behavior of certain of these solutions upon electrolysis.

If, then, solutions of certain salts are alkaline because of hydrolysis, and others are acid, it follows that in titrating an acid

or alkali under conditions that will form such salts, or in titrating the free acid or base present in solutions containing these salts, it is necessary to employ an indicator which will produce a definite color change or end point when the base and acid are equivalent to each other and not at the true neutral point. $[H^+] = 10^{-7}$. For simplicity we may state that titrations of the total acidity of a weak acid, or in the presence of a weak acid, such as acetic or carbonic acid, should be made with an indicator such as phenolphthalein, which changes to pink only when the solution is appreciably alkaline (*i.e.*, contains a slight excess of hydroxyl ions). For titrations of a weak base, such as ammonium hydroxide, or of an acid in the presence of ammonium salts, or in the presence of salts such as copper sulphate, zinc sulphate, etc., an indicator such as methyl orange should be employed, which changes color when the solution is appreciably acid. Consideration of these principles will explain the failure to get reliable results when the wrong indicator is used. Unfortunately the colors of many plating solutions may mask those of the indicators, but in such cases, with some care, an approximate end point may often be obtained. Thus it is possible to titrate the free sulphuric acid in a copper sulphate solution by using methyl orange, in the presence of which the solution undergoes, at the end point, a color change from purple to green, instead of the customary red to yellow.

CHAPTER IV

ELEMENTARY PRINCIPLES OF CHEMICAL ANALYSIS

1. SAMPLING

The most fundamental condition for securing reliable analytical results by any method whatever is care in taking the sample of the solution. In order that the result of the analysis may have any real significance the following precautions must be taken.

(*a*) The solution in the tank should be made up, by the addition of water if necessary, to a definite volume, as indicated by a fixed mark on the inside of the tank. It is very misleading to analyze a solution which at one time is 26 in. deep and a week later is 22 in. deep, as any apparent change in concentration may be due entirely to evaporation and not to the reactions produced by the electrolysis. For accurate results in research work, the volume of the anodes and cathodes should be taken into account. For most purposes, however, we may assume that they remain nearly constant and do not therefore introduce appreciable errors.

(*b*) After diluting to the fixed mark, the solution should be thoroughly mixed, in order to insure that the sample taken represents the average composition of the entire bath. In many cases where still solutions are employed, it is objectionable to stir up the solution, because the sediment is thereby mixed through the bath, and may cause rough deposits. In such cases the solutions should be mixed at the close of the day so that the sediment in the tanks may settle out overnight. (Entirely apart from the sampling, it is desirable to stir up solutions daily or at least once a week, *e.g.*, on Saturday, as any tendency of the solution to "stratify" into layers of different concentration or composition is certain to cause irregular deposition.) When it is necessary to take a sample at a time when mixing of the solution is not feasible, a fairly representative portion may be secured by inserting slowly into the solution in a vertical position a glass tube about 1 cm. (0.4 in.) in inside diameter. A

finger is then placed over the upper end of the tube, the latter lifted out of the solution, and the liquid allowed to run into a bottle. Portions should be taken from different parts of the tank and well mixed in the sample bottle.

(*c*) The sample should be placed in a clean bottle, which should either be dry, or if wet should be first rinsed out with some of the solution from the tank to be tested. It should always be tightly stoppered and labeled with the number of the tank and the date of sampling. Generally a bottle holding 4 fluid oz. (about 120 c.c.) will be sufficient for routine analyses.

(*d*) It is usually preferable not to filter the sample at once, especially if it is to be sent to a laboratory, since the nature and amount of the sludge present may be of interest. Before making an analysis however, the entire sample should be filtered.

2. QUALITATIVE ANALYSIS

A chemical analysis of any material is designated as *qualitative* if it is desired merely to learn what elements are present in the substance, and *quantitative* if it is desired to determine the percentage or concentration of one or more of the elements present.

Qualitative analysis is often of value in detecting the presence in plating solutions, or in materials used in their preparation, of impurities or objectionable constituents. In general, such tests are of only limited value because in commercial chemicals such as are necessarily employed, small amounts of many impurities are almost certain to be present, and their detection is not sufficient cause for rejection of the material unless it can be shown that the impurities are present in such a proportion as to cause an appreciably injurious effect. With a little care, however, it is often possible to make a qualitative test in such a way as to determine roughly the relative amount of an impurity as compared with similar material of known or adequate purity. As an illustration, it is possible to make a comparative test of the amount of copper present in two samples of nickel salts, or of nickel solutions, by adding to approximately equal amounts of the solutions a small amount of dilute hydrochloric acid, followed by some hydrogen sulphide water. (The latter may be prepared by adding to some dilute sodium sulphide solution dilute hydrochloric acid until litmus paper is just turned pink.) If copper is present a dark or black precipitate will be

formed, and by comparison it is easy to determine roughly whether the one sample contains decidedly more or less copper than the other. Such a test, although carried out in a qualitative way, may thus become semi-quantitative.

The underlying principle of qualitative analysis is the treatment of a solution of the substance in regular order with various chemicals or reagents, which produce with certain elements or groups of elements characteristic reactions, such as the formation of a precipitate, which has a definite color or a definite solubility in certain chemicals or "reagents." By such treatments it is possible to determine whether any of the elements of a certain group are present, and if so, to make additional tests to detect the specific elements. For detailed methods of qualitative analysis, regular texts should be consulted. When it is possible by a simple test of plating materials to determine the presence or absence of some deleterious substance, the test will be briefly described in the appropriate place in this text.

3. QUANTITATIVE ANALYSIS

Most analytical work in connection with plating is quantitative, for the purpose of determining whether the solution contains the desired amounts of one or more constituents, and if not, what changes in or additions to the solution should be made. A complete quantitative analysis, *i.e.*, the determination of all the constituents of the solution, is practically never required, and fortunately so, because such an analysis would require more time and expense than would usually be warranted, and might indeed be impossible, even with the most refined methods. In general, in quantitative analysis, the elements (or in some cases the acid radicals) are determined, and from them the amounts of the compounds present in the solution are calculated. Suppose, for example, that a nickel solution was prepared from nickel sulphate (single nickel salt), nickel ammonium sulphate (double nickel salt), sodium chloride (common salt), and boric acid. For control work, the analysis of such a solution would usually consist in the determination of nickel, ammonia, and chloride. From these three determinations, the content of the first three of the above compounds can be readily calculated and hence it would be unnecessary to determine either the content of sodium or of sulphate. The boric acid would rarely be determined, because the methods for its estimation are rather lengthy and

usually unreliable. Fortunately its concentration is limited by its low solubility, and as boric acid is a very weak acid, appreciable variations in concentration have little effect.

Most methods of quantitative analysis may be classed as gravimetric, volumetric or colorimetric.

(a) **Gravimetric Analysis.**—*Gravimetric* methods consist in general in the formation, in the solution, of an insoluble precipitate containing the element to be determined, the removal of that precipitate by filtration, the washing of the precipitate to remove other compounds from it, and the drying or ignition of the precipitate to form a substance of definite weight and composition, from which weight the amount of the element in question may be calculated. As an illustration of a gravimetric method frequently employed, we will describe the estimation of the amount of chlorine present as chloride in a nickel solution. It is important to note that such an analysis indicates only the amount of chlorine present as chloride in the solution, and gives no indication of whether the chlorine was added in the form of nickel chloride, sodium chloride, or ammonium chloride. For convenience in the following illustration, we will assume that sodium chloride was used in the preparation of the solution.

A definite volume of the solution, *e.g.*, 10 c.c., is measured by means of a pipette, and is run into a clean beaker having a capacity of about 250 c.c. Distilled water is added until the volume is about 150 c.c., and a few drops of nitric acid are added. The solution is then carefully heated nearly to the boiling point, when a 0.1 *N* solution of silver nitrate (containing 17 g./l. of $AgNO_3$) is added slowly. The solution is stirred vigorously for a few minutes, and as the white precipitate (of silver chloride) settles out, more silver nitrate is added, until no further precipitate is produced. The beaker with the solution is then allowed to stand a few hours (or preferably overnight). In the meantime a layer of asbestos, which has been purified and suspended in water, is placed in a porcelain Gooch crucible, *i.e.*, a crucible in the bottom of which are a number of fine holes.[1] The asbestos

[1] For most gravimetric analyses, *e.g.*, the determination of sulphur as barium sulphate ($BaSO_4$), the precipitate is filtered upon a quantitative or "ashless" filter paper, which is then dried and ignited in a porcelain or platinum crucible. This method cannot, however, be used with silver chloride, which would be reduced to metallic silver when heated with the carbon of the filter paper.

is introduced, in the form of a "pulp" in water, into the crucible, which is supported in a suction flask; and by suction a firm mat of asbestos is produced in the bottom of the crucible. The crucible with the asbestos is then dried for 1 hr. in an oven heated to 130°C. (266°F.). It is then permitted to cool in a desiccator (a closed vessel containing a drying agent, such as calcium chloride) and is weighed upon an analytical or other sensitive balance. The solution containing the precipitated silver chloride is then filtered through this asbestos filter, using suction as before. All the precipitate is transferred to the filter, and both the precipitate and the filter are washed with a very dilute solution of nitric acid in order to remove from the silver chloride any silver nitrate, sodium nitrate, or nickel salts. The crucible and precipitate are dried and weighed as before, and the increase in weight represents the amount of silver chloride (AgCl) produced. Suppose that 10 c.c. of the nickel solution were used, and the crucible and asbestos weighed 17.043 g., and with the silver chloride it weighed 17.364 g. Then the weight of silver chloride is $17.364 - 17.043 = 0.321$ g. The calculation of the amount of sodium chloride present in the solution is similar to that explained on page 16. If the equation for the precipitation is:

$$\underset{}{AgNO_3} + \underset{58.5}{NaCl} = \underset{143.5}{AgCl} + \underset{}{NaNO_3}$$

it follows that for each 143.5 parts of silver chloride produced, there was present 58.5 parts of sodium chloride; therefore the sodium chloride present in 10 c.c. is equal to

$$\frac{58.5}{143.5} \times 0.321 = 0.131 \text{ g.}$$

Therefore in 1,000 c.c. of solution there is present $100 \times 0.131 = 13.1$ g./l., or $13.1 \times 0.134 = 1.75$ oz./gal. of sodium chloride.

From the above illustration (which is by no means an exceptionally difficult method) it is obvious that the application of gravimetric methods involves the use of rather elaborate equipment, including an expensive balance, and that it requires not only considerable time to complete, but also a large amount of attention from the analyst. For these reasons simpler methods, such as volumetric methods, are employed wherever possible, especially when, as in plating control work, no very high degree of accuracy is required.

The *electrolytic* methods of determining metals are gravimetric methods, which are, however, free from many of the objections to other gravimetric methods, and are especially suited to the estimation of the metal content of plating solutions. Electrolytic methods depend upon the deposition of the metal present in the solution (*e.g.*, copper or nickel) upon a weighed cathode, using an insoluble anode, *i.e.*, one which is not attacked or dissolved by the solution during electrolysis. In such methods it is obviously necessary to employ conditions which will insure the deposition of all the metal in the solution. The principal objection to the general application of electrolytic methods in commercial work is the expense of platinum electrodes, which are necessary for work of high accuracy. Where many determinations are to be made, this expense is fully justified, and they should always be employed if possible. In many cases, especially for electrolysis in neutral or alkaline solutions, a copper cathode may be employed, and a spiral of platinum wire, which weighs only a few grams, may be used as the anode. In certain determinations, as, *e.g.*, in the deposition of copper from an acid solution, a lead anode may be used, but platinum is preferable.

In any case it is necessary to employ a fairly sensitive balance to weigh the cathode before and after the deposition. A very expensive balance is not necessary, however, and one that is sensitive to 1 mg., and which can be bought at a reasonable price, will answer all probable requirements. The simplest method of determining metals electrolytically is with stationary electrodes. Current may be secured directly from the plating busbars, but a storage cell will be found more constant and convenient.

As a typical illustration of an electrolytic method, the determination of the nickel content of a nickel plating solution will be described in detail. The apparatus required consists of:

(1) A cathode, which may consist of a cylinder of platinum gauze about 5 cm. (2 in.) high and 5 cm. (2 in.) in diameter, to which is attached a piece of platinum wire. Such a gauze electrode will usually weigh about 25 g. A satisfactory cathode can be made much more cheaply from copper gauze, with a copper wire attached. In making a copper gauze cathode it should be fastened together entirely with copper wire, using no solder. No great care is warranted in its preparation, because it will usually be best to discard it after a few determinations.

The purpose in using the gauze rather than a smooth piece of metal is to provide a larger area to receive the deposit, and thus permit the use of a higher current and of a shorter period for a determination. The exact area of a gauze electrode will depend upon the size of the wire and of the spaces, but, for simplicity, in calculating the average current density we may assume that the area is at least twice that of a piece of foil of the same outside dimensions. Shortly before using, the cathode should be cleaned, rinsed in distilled water, and dried. With a platinum cathode this drying may be accomplished by heating directly in a bunsen flame. A copper cathode should be rinsed with water and then with alcohol, and then dried quickly in a warm place. The cathode should be allowed to cool (preferably in a desiccator) and then weighed. For rinsing the cathode, ethyl (grain) alcohol denatured with methyl (wood) alcohol (according to formula No. 1 of the U. S. Internal Revenue Specifications) may be used.

(2) An anode of platinum wire, twisted into a spiral about 1 cm. (0.4 in.) in diameter and 4 cm. (1.6 in.) in height. This will require about 20 cm. (8 in.) of platinum wire, which, if of No. 22 gage, will weigh about 1.5 g.

(3) A beaker holding about 250 c.c. The tall-form beaker, without a lip, will be most convenient.

(4) A rheostat, such as may be cheaply made by wrapping nichrome or other resistance wire around a wood or metal frame covered with asbestos.

(5) An ammeter, with a range from 0 to 5 amp.

(6) A storage battery or other source of direct current with an electromotive force of about 4 to 6 volts.

The entire set up would be arranged as shown in Fig. 1.

Frequently it will be found convenient to allow the electrolysis to run overnight, in which case the rather long period (usually 3 to 5 hr. or more) required for electrolysis with stationary electrodes is not a serious objection. Where, however, time is an essential consideration, it is possible to reduce this period greatly by suitable agitation of the solution. Such agitation may be produced by rotating the anode, the cathode, or a glass stirrer by means of a small motor, by electromagnetic stirring, or by bubbling air through the solution. Under these conditions a higher current density may be employed, and hence deposition may be completed in a shorter period. By the use of the higher

current the solution is also heated appreciably, which reduces the resistance and still further increases the current density (produced by a given voltage). Moreover, smoother deposits are usually produced in the warmer solutions.

To carry out a nickel determination, a sample of solution sufficient to contain not more than about 0.5 g., or less than 0.2 g., of nickel should be used. Thus if the solution contains approximately 15 g./l. (2 oz./gal.) of metallic nickel, a 25-c.c. sample will contain about 0.38 g. of nickel. For stronger solutions, a 10-c.c. sample is sufficient. The sample is measured by means of a pipette and is introduced into a 250-c.c. beaker, diluted slightly with water, and about 5 g. of ammonium sulphate is added. Concentrated ammonium hydroxide is then

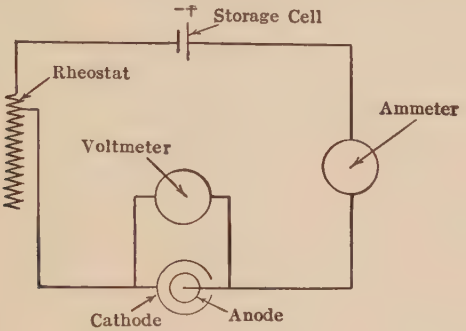


FIG. 1.—Diagram of Equipment for Electroanalysis.

added, while the solution is stirred, until a deep blue solution is produced. If a brownish precipitate of ferric (iron) hydroxide separates, it is not objectionable. After a blue solution is produced, about 20 c.c. more of the ammonium hydroxide is added, and the solution is diluted to about 200 c.c.

Electrolysis is then started with a cathode current density of about 0.25 amp./dm.^{2} (0.016 amp./sq. in.) in still solutions, or about 1 amp./dm.^{2} (0.06 amp./sq. in.) in a well-agitated solution. Thus a plain cylindrical cathode 5 cm. (2 in.) in diameter and 5 cm. (2 in.) high would have an area (on one side) of about 80 cm.^{2} or 0.8 dm.^{2} (13 sq. in.). For a gauze cathode we may assume twice this area, *i.e.*, 1.6 dm.^{2} (25 sq. in.), and therefore a total current of about 0.4 amp. would be used in still solutions and about 1.6 amp. in agitated solutions. With

the average amount of nickel likely to be present, deposition will probably be complete in about 4 hr. in a still solution and in about 1 hr. in an agitated solution.

The disappearance of the blue color of the solution will indicate when most of the nickel is deposited, but this is not a sufficiently delicate test for analytical purposes. By arranging the cathode so that it is not entirely immersed in the solution, and by adding a small amount of water to the solution when the electrolysis is apparently complete, it is possible to determine whether on continued electrolysis more nickel is deposited on the cathode. This may, however, be difficult to observe on a platinum cathode.

The most delicate test is to remove a few drops of the solution (after the blue color has entirely disappeared) and to add to it a few drops of a 1 per cent alcoholic solution of dimethylglyoxime. If a pink color or precipitate is produced, all the nickel has not been removed, and electrolysis should be continued till no pink color is produced upon repeating this test.

When deposition is complete the cathode is removed, rinsed quickly with distilled water and with alcohol, and allowed to dry in a warm place and to cool in a desiccator. After the electrode is cool it is reweighed, and from the increase in weight the nickel content is readily calculated. Suppose, *e.g.*, that a 25-c.c. sample of the nickel solution was used, and the increase in weight of the cathode was 0.306 g.; then the solution contained $0.306 \times \frac{1,000}{25} = 12.2$ g./l. (1.63 oz./gal.) of metallic nickel. The method of calculating from these and other data the content of single or double nickel salts is explained on page 263.

(b) **Volumetric Analysis.**—*Volumetric* methods of analysis are frequently applicable to plating solutions. All volumetric methods depend upon the addition of a standard solution which will react in a definite way with the constituent to be determined. From the known strength of the standard solution and the volume of it required to react completely with the constituent in question, the amount of the latter may be readily calculated. Thus if under appropriate conditions (page 261) it was found that it required 26.8 c.c. of a certain sodium cyanide solution to react completely with the nickel present in 10 c.c. of a plating solution, and if it had been previously found that each cubic centimeter of the cyanide solution was equivalent to 0.0052 g. of nickel, then

the 10-c.c. sample contained $26.8 \times 0.0052 = 0.139$ g. of nickel; and the solution contained $0.139 \times 100 = 13.9$ g./l. = 1.86 oz./gal. of nickel.

The simplest volumetric methods are those used in *acidimetry* and *alkalimetry*, *i.e.*, the determination of the amount of acid or alkali in a given solution. Such methods depend upon the neutralization of an acid by an alkali or vice versa, using an appropriate indicator to determine when they are present in equivalent amount (see page 30).

Another common type of volumetric methods is that depending upon the *oxidation* or *reduction* of the substances employed. Thus the most common method for the determination of iron in solutions consists in the preliminary reduction of the iron salt to the ferrous state (*i.e.*, a valence of Fe^{+II}) by a reducing agent such as metallic zinc; and the addition of a standard potassium permanganate ($KMnO_4$) solution (an oxidizing agent) to reoxidize the ferrous salt to ferric salt (Fe^{+III}). As soon as a slight excess of permanganate is added, a pink color is produced in the solution, which color serves as the end point. If the strength of the permanganate is known, the amount of iron present can be readily calculated.

In another class of volumetric methods, an appropriate solution is added to *precipitate* the desired constituent. Thus in the volumetric determination of zinc, which may be applied to a sulphate zinc plating solution, potassium ferrocyanide, $K_4Fe(CN)_6$, is added from a burette. A white precipitate of potassium zinc ferrocyanide is formed, and the end point is determined by removing a drop of the solution and mixing it on a porcelain plate with a solution of uranium acetate, which produces a brown color as soon as an excess of potassium ferrocyanide is added. In this operation an "outside indicator" is employed, as distinguished from the preceding methods, in which the end point is determined by an "inside indicator," *i.e.*, by a color change within the solution.

Certain volumetric methods for the determination of cyanides are of special interest to platers. These methods depend upon the formation of soluble double cyanides, such as sodium silver cyanide, which may be written NaCN.AgCN or $NaAg(CN)_2$. When to a solution containing sodium cyanide (NaCN), silver nitrate is added, it first combines to form the above compound, and as soon as more silver nitrate is added than is required for

this compound, a white precipitate of silver cyanide (AgCN) is formed, and serves as the end point of the titration. A sharper and more definite end point is usually obtained by having present a small amount of potassium iodide, which forms at the end point, a yellowish precipitate of silver iodide (KI).

The principal instruments required for volumetric analysis are two 50-c.c. burettes, a 10 and a 25-c.c. pipette and a 500 or a 1,000-c.c. graduated flask. In addition, a fairly sensitive balance is necessary for weighing the materials used in the preparation or standardization of the solutions, but this does not have to be used frequently and may be dispensed with if standard solutions can be secured from a reliable chemist or dealer. A pipette, which is used to measure samples of solution, is graduated to *deliver* the designated volume when it is filled up so that the lower edge of the meniscus is on the graduation mark, and when it is allowed to drain with the tip touching the side of the beaker. *The contents should not be blown out.* A burette is graduated to deliver the specified volumes when the solution is allowed to run out not faster than a certain rate, for which the burette tip is adjusted by the manufacturer. A graduated flask is calibrated to *hold* the specified volume when the lower edge of the meniscus is on the graduation mark. All volumetric apparatus is calibrated for a definite temperature, usually either 15°C. (59°F.) or 20°C. (68°F.). For approximate work it is not necessary to use the apparatus at exactly that temperature, but the standard solutions and the sample to be analyzed should always be measured at approximately the same temperature. Thus a portion of a warm plating solution should always be cooled to room temperature before the sample for analysis is measured.

In all volumetric methods it is necessary to know or determine the strength of the standard solution. In many cases, especially in acidimetry, it is convenient to use solutions which are normal or of some definite normality, *e.g.*, half normal or tenth normal. As explained on page 27, equal volumes of such solutions, *e.g.*, of acid and alkali, are exactly equivalent to each other, and hence their use may in some cases reduce the calculations. In other analyses it is found convenient to adjust the strength of the solutions so that 1 c.c. is exactly equivalent to 0.001 g. or 0.01 g. of the particular metal. In almost every case, however, it is necessary to determine by some independent means the strength

of the solution, *i.e.*, to *standardize* it. If this operation is carried out and 1 c.c. of a certain standard alkali solution is found to be equal to 0.0515 g. of sulphuric acid (and is therefore 1.05 *N*), it is generally just as easy to use this factor as to adjust the concentration by dilution so as to make the solution exactly normal (*i.e.*, 1 c.c. equal to 0.049 g. of sulphuric acid), or for numerical simplicity to make it exactly equal to 0.05 g. of sulphuric acid. Especially if the use of a slide rule is mastered, it is as convenient to employ one factor as another.

One important condition in all volumetric analysis is to have the standard solutions of such strength that for a convenient sample of the plating solution (usually 10 to 25 c.c.) a reasonable volume of the standard solution will be required, preferably between 20 and 30 c.c. If too strong a solution is employed and, *e.g.*, only 5 c.c. is used in a titration, it is difficult to get approximately correct results, since an uncertainty of only 0.1 c.c. will cause an error of 2 per cent in the result. On the other hand, if over 50 c.c. of a titrating solution is required, the burette must be refilled, and usually no greater accuracy is secured.

The strength of a standard solution may be determined directly or indirectly. Thus in acidimetry it is possible to prepare a standard (*e.g.*, normal) solution of sodium carbonate by weighing out accurately the proper amount of pure sodium carbonate (Na_2CO_3) which has been dried just previously at a temperature of about 130°C. (264°F.). To make a normal solution of sodium carbonate requires exactly 53 g. of pure dry sodium carbonate (Na_2CO_3) dissolved in water and diluted to a volume of 1 l. (not dissolved in a liter of water). If such a solution is prepared, it is possible by a series of simple comparative titrations to determine the strength of other acid or alkaline solutions. Thus we may determine the volume of sodium carbonate solution required to neutralize 25 c.c. of a sulphuric acid solution of approximately equal strength, and thus determine the exact strength of the sulphuric acid. This, in turn, can be used to standardize a solution of ammonium hydroxide, etc.

The use of a single primary standard for a number of volumetric solutions possesses great advantages from the standpoint of simplicity and convenience. Such a standard is metallic silver, which can readily be obtained in the form of thin foil, having a purity of 99.9 per cent (so-called "999 pure"). By

its use it is possible to standardize the solutions of silver nitrate, hydrochloric acid, sodium hydroxide, and sodium cyanide, which are useful for numerous analytical determinations. The following directions for tenth normal solutions can be applied to the preparation of solutions of other strengths by the use of proportional weights of the various substances.

Preparation of Standard Solutions. (1) *Tenth Normal Silver Nitrate.*—Weigh out exactly 10.8 g. of pure silver. (If this is in the form of thin foil it is easy to cut it with shears to obtain the above amount within 0.05 g.) Place this in a 250-c.c. beaker, cover it with a little water,[1] place a watch glass over it, and add slowly about 50 c.c. of dilute nitric acid (1–1). Too rapid action and loss of material may be avoided by adding the nitric acid carefully and by setting the beaker in a vessel of cold water. When the action has ceased, rinse down the cover glass and sides of the beaker with water. Evaporate the solution to dryness on a steam bath or over a beaker of boiling water. When the evaporation is complete, rinse down the sides of the beaker with about 25 c.c. of distilled water from a wash bottle and again evaporate to dryness, to expel all the excess nitric acid. Dissolve the residue of silver nitrate in water, and dilute it in a volumetric flask to 1 liter.

Note.—If pure silver is not available, crystallized silver nitrate may be used. It should first be dried by heating in an oven to 110°C. for 1 hr. and then allowed to cool in a dessicator. Exactly seventeen grams of the dry salt is weighed out, dissolved in water, and diluted to 1 liter.

(2) *Hydrochloric Acid.*—To prepare a solution which is approximately 0.1 *N*, dilute about 9 c.c. of pure concentrated hydrochloric acid (specific gravity 1.2) to 1 liter.

(3) *Sodium Hydroxide.*—Dissolve about 4.5 g. of pure stick sodium hydroxide in water and dilute to 1 liter.

(4) *Sodium Cyanide.*—Dissolve about 5.5 g. of pure sodium cyanide in water and dilute to 1 liter.

(5) *Methyl Orange Indicator.*—Dissolve 0.25 g. of the indicator in about 250 c.c. of water.

(6) *Sodium Chromate Indicator.*—Dissolve 2 g. of neutral sodium chromate (Na_2CrO_4—not dichromate) in 100 c.c. of water.

[1] In this and all other analytical operations distilled water should be used.

(7) *Potassium Iodide Indicator.*—Dissolve about 8 g. of potassium iodide (KI) in 1 liter of water. The solution is then about 0.05 *N*.

Standardization of Solutions.—The titrations should be made in duplicate, and the average of the two results taken. If duplicates do not agree within 1 per cent, the operations should be repeated until the cause of the disagreement is determined and overcome.

(1) *Comparison of Hydrochloric Acid and Sodium Hydroxide.*—Fill two burettes with the acid and alkali respectively, and run about 20 c.c. of the sodium hydroxide solution into a 200-c.c. flask. Dilute the solution to about 50 c.c., add one drop (no more) of the methyl orange solution, and titrate slowly with the acid until one drop of the acid turns the solution from yellow to orange-red. If this end point is passed too rapidly, add sufficient alkali to restore the yellow color and again titrate with acid, drop by drop, till the color changes. Note the volume of each solution required. Save the solution obtained at the end of the titration. Determine the ratio by dividing the number of cubic centimeters of hydrochloric acid by the number of cubic centimeters of sodium hydroxide used in titration. Thus if 20.2 c.c. of hydrochloric acid and 18.9 c.c. of sodium hydroxide are used, the sodium hydroxide is the stronger, in the ratio of $\frac{20.2}{18.9} = 1.07$.

(2) *Determination of the Strength of the Hydrochloric Acid.*—This can be accomplished by titrating with the silver nitrate solution a portion of the hydrochloric acid exactly neutralized with alkali. For this purpose we can therefore use the solution obtained in the preceding titration, and which is just slightly pink or orange in color. To this solution add about 1 c.c. of the sodium chromate indicator and then add the standard silver nitrate solution slowly from a burette till, after stirring, a faint permanent red precipitate is produced. To obtain the relative strength of the hydrochloric acid, divide the volume of silver nitrate required by the volume of hydrochloric acid used in the first titration. Thus if 20.2 c.c. of hydrochloric acid were used and 22.1 c.c. of silver nitrate were required, the hydrochloric acid is $\frac{22.1}{20.2} = 1.09$ times as strong as the silver nitrate. Since, however the silver nitrate as prepared was 0.1 *N*, the hydrochloric

acid must be $0.1 \times 1.09 = 0.109$ *N*. Similarly, the sodium hydroxide, which was found to be 1.07 times as strong as the hydrochloric acid, is $1.09 \times 1.07 = 1.17$ *N*.

(3) *Standardization of Sodium Cyanide.*—Fill one burette with the sodium cyanide solution and the other with silver nitrate solution. Run into a 200-c.c. flask about 30 c.c. of the sodium cyanide solution, add 10 c.c. of the potassium iodide solution, and dilute to about 75 c.c. Add the silver nitrate solution slowly, with constant shaking, until a faint permanent yellowish precipitate is produced. Note the ratio between the volume of silver nitrate and sodium cyanide, and calculate the relative strengths of the two. Multiply by 2 the *apparent* normality of the sodium cyanide as thus calculated, to obtain its true normality. This is necessary because in the reaction

$$AgNO_3 + 2NaCN = NaAg(CN)_2 + NaNO_3$$

two equivalents of sodium cyanide are required for each one of silver nitrate.

If in this titration, 30.3 c.c. of sodium cyanide require 16.2 c.c. of silver nitrate, the sodium cyanide is *apparently* $\frac{16.2}{30.3} = 0.535$ times as strong as the silver nitrate, but is *actually* $2 \times 0.535 = 1.07$ times as strong; therefore it is 0.107 *N*.

For most titrations involving the oxidation or precipitation of metals it is preferable to standardize the solutions by using definite weighed amounts of the pure metals, which are dissolved in appropriate acids and are then titrated under the same conditions of temperature, concentration, acidity, etc., as are to be used in the regular determinations. There is usually no difficulty in securing, for such standardizations, metals which have a purity of 99.5 per cent or better.

Electrometric Titrations.—In certain volumetric titrations, especially those involving oxidation and reduction, the change in the potential of a suitable electrode is used to detect the end point. A simple and customary application of this method is in the titration of chromic acid with ferrous sulphate, in the analysis of chromium plating baths (p. 308). The apparatus consists of a platinum wire and a calomel half-cell, which dip into the beaker containing the solution to be titrated. The latter is stirred, preferably with a mechanical stirrer, while the ferrous sulphate is run in from a burette. Just as soon as the ferrous sulphate has

completely reduced the chromic acid, there is a sudden change in the potential of the platinum electrode with respect to the calomel electrode, which is shown by a large movement of the galvanometer connected between them. This point is the end point of the titration.[1]

(c) **Colorimetric Analysis.**—If a plating solution is colored, or if it forms some characteristic color when a definite reagent is added, and if the strength of this color depends upon the concentration of the metal salt present, the latter can be determined by comparing the color of the solution with some known standard. Thus a copper sulphate solution is blue, and for practical purposes the intensity of the blue color depends only upon the concentration of the copper, and is not influenced by the concentration of sulphuric acid. Similarly the green color of a simple nickel solution depends only on the concentration of nickel in it, and is not measurably affected by such salts as ammonium, sodium or magnesium sulphate or chloride. If, however a substance such as sodium citrate is added to a nickel bath (*e.g.* for plating on zinc) it produces a bluish-green color, which is not directly comparable with the usual green color. The color of chromic acid is a typical orange red, but when basic chromium compounds or compounds of iron are present, it is brownish or nearly black. Simple colorimetric methods are therefore not applicable to chromium plating baths, though they might be applied to determine the total chromium content after oxidizing the chromium entirely to chromic acid; or to determine the amount of trivalent chromium present.

In general the principle of all colorimetric methods is the comparison of the color of the unknown sample with that of a standard of known concentration and color. This principle is employed in a very rough way by many platers and electrotypers, who keep a sample of their original copper or nickel solution in a bottle to serve as a "standard," with which at intervals they compare the color of a sample from the tank.

The problem of making actual colorimetric measurements resolves itself into (*a*) the preparation of standard solutions and (*b*) suitable equipment and methods for making the comparisons. The preparation of standard solutions with moderate accuracy,

[1] Details of various electrometric titrations will be found in "Potentiometric Titrations," by J. M. Kolthoff and N. H. Furman, published by John Wiley and Sons, New York, 1926.

e.g. about 5 per cent, is usually not difficult. Thus clean, clear crystals of "C.P." copper sulphate ($CuSO_4.5H_2O$) may safely be assumed to contain 25.4 per cent of metallic copper. Chemically pure nickel sulphate crystals may consist either of $NiSO_4.7H_2O$, with 20.9 per cent Ni, or $NiSO_4.6H_2O$ with 22.3 per cent Ni, or of a mixture of the two. If the salt is assumed to contain 21.5 per cent of metallic nickel, no error greater than about 3 per cent (of the nickel) is likely to enter. Appropriate weights of these salts may be dissolved in a definite volume to produce strong stock solutions which may then be diluted accurately to produce less concentrated standards. Where a higher accuracy, *e.g.*, 1 per cent or better, is required, it is necessary to determine the strength of the standard solution by a careful analysis, and to adjust it accordingly.

The strong standard solution should be at least as concentrated in metal as the strongest solution likely to be used in electroplating. Copper and nickel plating solutions are usually less than two normal (2 *N*). Solutions of this strength contain respectively 63.6 g./l. (8.5 oz./gal.) of metallic copper, and 58.7 g./l. (7.9 oz./gal.) of metallic nickel. The former requires exactly 250 g./l. (33.5 oz./gal.) crystallized copper sulphate, and the latter 272 g./l. (36.4 oz./gal.) of nickel sulphate.

Simple color standards can be prepared in small test-tubes of equal inside diameter, which should preferably be about 10 to 15 mm. (0.4 to 0.6 in.). Into each of these is introduced a measured volume of the standard solution, and the exact volume of water required to produce the desired concentration. Suppose each tube holds 20 c.c. up to a definite mark. Then into one tube may be placed 20 c.c. of the 2 *N* solution; into another 10 c.c. of the 2 *N* solution and 10 c.c. of water, thus producing a *N* solution, etc. In some cases it may be necessary to make up only a few standards, differing *e.g.* by steps of 10 per cent from the strength desired in the bath. Thus if the bath is about *N* in metal, five standards might be prepared that are respectively 0.8, 0.9, 1.0, 1.1, and 1.2 *N*. With such standards the strength can be estimated to within 5 per cent. If tightly stoppered, preferably with waxed corks, the tubes will retain their concentration for periods of a month or more. If they are in sealed glass tubes they keep indefinitely.

To determine the strength of a nickel or copper solution, all that is necessary in principle is to place some of the unknown sample in

a tube of the same diameter and hold it alongside one or another of the standards, until they match in color when viewed against a uniform light, such as a northern sky. Greater accuracy is obtained by holding the unknown sample in a suitable block between two standards, which are changed until the unknown matches one, or is intermediate between the two. If then a certain nickel solution matches a tube containing N nickel sulphate, the unknown is also N in nickel, *i.e.*, it contains 30 g./l. or 4 oz./gal. of metallic nickel. If it is intermediate between standards that are respectively 0.9 and 1.0 N, it is approximately 0.95 N, *i.e.*, it contains 28.5 g./l. or 3.8 oz./gal. of metallic nickel.

With most colors such as yellow, pink and blue, in not too high a concentration, the average eye can match concentrations within about 5 per cent. The eye is much less sensitive to green, however, and it is often difficult to detect directly differences in concentrations of nickel solutions as great as 15 per cent. This difficulty can be overcome by viewing the nickel solutions through a pink screen, which "optically neutralizes" the green color, *i.e.* tends to produce a white or gray color. This principle is employed in one commercial test set in which sealed tubes containing a pink solution of a salt such as cobalt sulphate are used in connection with standard tubes containing both nickel sulphate and the pink salt. In another device of the wedge type, a strip of pink celluloid is used to neutralize the green color. By this expedient it is possible to obtain a match within about 5 to 10 per cent, which in many cases is sufficient for works control.

These colorimetric methods have been discussed at some length even though they are not very accurate, and at present are not available in entirely satisfactory forms. Their simplicity justifies their further development, so that they may be as conveniently applied as the colorimetric methods for measuring pH. If such methods were available, daily colorimetric control of the copper, nickel, or chromium content of a plating solution within 5 per cent would usually be entirely adequate for commercial operation. Occasional chemical analyses should then be made in order to detect errors due to any change in the standards, or to contamination of the plating baths with impurities that might affect the color.

CHAPTER V

PRINCIPLES OF ELECTRICITY

The most convenient way to explain the relation of the various factors which determine the flow of direct current in metallic conductors is through the use of the time-honored analogy to the flow of water. This analogy is only superficial and has distinct limitations in its applications, but nevertheless it is so helpful that its use is fully justified.

For water to flow through a pipe, a certain *pressure* is necessary or, more strictly speaking, a certain difference in pressure between two ends of the pipe, or two points within the pipe. The *rate* at which the water flows through the pipe is *directly* proportional to the magnitude of this pressure difference, and is *inversely* proportional to the resistance offered by the pipe to the flow of water. Thus if in one case the pressure (or "head") of water is twice as great as in another case, the water will flow through the pipe twice as rapidly. If, on the other hand, one pipe has a resistance twice as great as another pipe, with a given pressure the water will flow only one-half (*i.e.*, 1 divided by 2) as rapidly through the pipe with high resistance as through that with low resistance. The resistance of any pipe to the flow of water is *inversely* proportional to its cross-section, *i.e.*, a small pipe offers more resistance than a large pipe. Similarly, the resistance is *directly* proportional to the length of the pipe; therefore the longer the pipe the greater the resistance. The resistance also depends upon the material of which the pipe is constructed and upon the smoothness of the inner surface of the pipe. The *quantity* of water that flows through the pipe in any given period is equal to the rate of flow, *i.e.*, the number of gallons per minute, multiplied by the number of minutes that the water flows. These facts regarding the flow of water in pipes may be expressed in the form of an equation:

$$\text{Current (rate of flow)} = \frac{\text{Pressure}}{\text{Resistance}}$$

or

$$\text{Gallons per minute} = \frac{\text{Feet (head of water)}}{\text{Resistance}}$$

(There is no simple unit of measurement which defines the hydraulic resistance of a pipe.)

If in the above illustration we substitute the equivalent electrical units, we find that an exactly similar relation holds true.[1] For a current of electricity to flow through a conductor, there must be a certain pressure or potential difference between the two points on the conductor. This electrical pressure, potential difference, or electromotive force (e.m.f.) is expressed in *volts* (V), and represented by E. The rate at which the current flows, which rate is measured in *amperes* (amp.), and usually represented by the symbol I, is *directly* proportional to this pressure and is *inversely* proportional to the resistance (R), which is dependent upon the size (cross section) length, and composition of the wire. The resistance of a metal conductor increases with its length, and decreases with a larger cross-section. Different metals have different resistivities, those of silver and copper being the lowest. This resistance is measured in ohms (Ω). The above relation, which is known as *Ohm's law*, may be expressed by the equation:

$$\text{Current} = \frac{\text{Electromotive force}}{\text{Resistance}}$$

or

$$I = \frac{E}{R}$$

or

$$\text{Amperes} = \frac{\text{Volts}}{\text{Ohms}}$$

or

$$\text{Amp.} = \frac{V}{\Omega}$$

As the current, e.m.f., and resistance in any electrical circuit, or *in any part of an electrical circuit*, are related to each other in accordance with the above equation, it follows that if in any case

[1] An objection sometimes made to the analogy between the flow of water and that of electricity is that electricity requires a complete circuit for its continued flow, and water apparently does not. This objection is not valid because for any continuous flow of water there must be a complete cycle, *i.e.*, the water pressure must be maintained by natural processes or by some mechanism for transporting the water from a lower to a higher level, or else flow ceases. In observing the flow of water we are accustomed, however, to think only of the downward flow, and not of that upward flow which is necessary to maintain the pressure or difference in level.

two of these quantities are known, the other one can be readily calculated. This equation may be expressed correctly in three forms:

(1) $I = \frac{E}{R}$ The current is equal to the e.m.f., divided by the resistance.

(2) $E = IR$ The e.m.f. is equal to the current multiplied by the resistance.

(3) $R = \frac{E}{I}$ The resistance is equal to the e.m.f. divided by the current.

The following simple examples illustrate the possible applications of these forms.

Problem.—If in a given circuit with a resistance of 0.02 ohms, an e.m.f. of 5 volts is applied, what current will pass?

$$I = \frac{E}{R} = \frac{5}{0.02} = 250 \text{ amp.}$$

Problem.—If through a certain busbar with a resistance of 0.003 ohms, a current of 600 amp. is flowing, what will be the potential drop (*i.e.*, the difference in potential or e.m.f. or "*IR* drop") between the ends of the bar?

$$E = IR = 600 \times 0.003 = 1.8 \text{ volts.}$$

Problem.—If across a certain contact in a circuit, a potential difference or e.m.f. of 0.01 volt is observed (by measurement with a millivoltmeter), when a current of 50 amp. is flowing, what is the resistance of the contact?

$$R = \frac{E}{I} = \frac{0.01}{50} = 0.0002 \text{ ohms.}$$

The values of the three fundamental electrical units are internationally defined in such terms that Ohm's law holds true in the form:

$$\text{Amperes} = \frac{\text{Volts}}{\text{Ohms}}$$

The **ampere** is defined as that current which, under specified conditions, deposits a definite weight (1.118 mg.) of silver in 1 second. This operation is carried out in a special apparatus known as a "silver coulometer" or "voltameter,"[1] in which a

[1] The term "voltameter," which is still frequently used as a synonym for "coulometer," should not be confused with "voltmeter."

silver nitrate solution is electrolyzed with a silver anode and a platinum cathode. Although under these conditions the deposition of silver is quantitative, the deposit is coarsely crystalline and not suitable for electroplating purposes. In practice, the current is measured in amperes by means of an instrument called an "ammeter" (page 184).

The **ohm** is defined as equal to the electrical resistance at 0°C. of a uniform column of mercury having a mass of 14.4521 g. and a length of 106.3 cm. The resistance is usually measured or calculated indirectly.

The **volt** is defined as that difference in potential which will produce a current of 1 ampere in an electrical circuit of which the resistance is 1 ohm. For practical purposes the volt may also be expressed in terms of the saturated Weston standard cell, the e.m.f. of which at 20°C. is 1.0183 volts. Thus in making potential measurements by means of a potentiometer a standard cell of known e.m.f. is always used as the basis of comparison. The e.m.f. is usually measured in terms of volts, by means of an instrument called a "voltmeter" (page 184).

The **quantity** of electricity that passes is equal to the current multiplied by the time, *e.g.*, to the number of amperes multiplied by the number of seconds. The scientific unit is the *coulomb*, which is the quantity of electricity that passes when a current of 1 amp. flows for 1 second. It is important to distinguish between the *rate*, *i.e.*, the number of amperes, and the *quantity*, *i.e.*, the number of coulombs, just as in the flow of water we must distinguish between the rate, or number of *gallons per minute*, and the *volume*, or the number of *gallons* that actually flow in any given period. This distinction is brought out in the two equivalent and correct statements that "1 ampere deposits 1.118 mg. of silver in 1 second," and "1 coulomb deposits 1.118 mg. of silver." The common commercial unit employed in electrodeposition is the *ampere-hour* (equal to 3,600 coulombs), which is equal to the quantity of electricity that passes when a current of 1 amp. flows for 1 hr. In recent years the expression "ampere minutes" has been frequently employed to express the current and time employed in plating. Thus if an article is plated with chromium for 3 min. at 100 amp. sq. ft., it has been plated for 300 amp. min./sq. ft.

The **power** expended in the passage of an electrical current is equal to the product of the applied e.m.f. and the current, *i.e.*,

the number of volts multiplied by the number of amperes. It is expressed in terms of the *watt*, which is the power involved when a current of 1 amp. is passed through a circuit by the application of 1 volt. The usual commercial unit is the *kilowatt*, equal to 1,000 watts. One horsepower is equal to 746 watts, or 1 kw. is equal to 1.34 hp. (This relation is useful in determining what horsepower a motor should have to drive a generator with an output of a certain number of kilowatts, page 173.)

The **energy** consumed in the passage of the current is equal to the power multiplied by the time, *e.g.*, watts multiplied by seconds, (in which case the energy is expressed in *joules*, each of which is equal to the energy consumed in applying 1 watt for 1 second). The usual commercial units are the *watt-hour* (equal to 3,600 joules) and the kilowatt-hour (equal to 1,000 watt-hr.). The kilowatt-hour is the usual basis of payment for electrical energy.

In general, in the electrodeposition of metals, a direct current of electricity is caused to pass through a solution between two metallic surfaces, from one of which metal is dissolved, and upon the other of which metal is deposited.

The solution through which the current passes is called the *electrolyte*.[1] It contains, in addition to water, a compound, usually a salt, of the metal to be deposited, and in most cases one or more other substances which are added to improve the conductivity of the solution or to influence the character of the deposit. The passage of a current through a solution is known as *electrolysis*.

The objects through which the current enters and leaves the solution are the *electrodes*. The electrodes from which the metal is dissolved, or upon which oxygen is discharged during electrolysis, are the *anodes*, which are usually designated with a plus or positive sign (+). Those upon which the metal (or

[1] The term "electrolyte" is now used with two distinct meanings. Many physical chemists designate as electrolytes those substances such as acids, bases and salts, which when dissolved form conducting solutions. Most physicists and electrochemists call the conducting solution the electrolyte. In a discussion of this subject (W. Blum, *Trans. Am. Electrochem. Soc.*, vol. 47, p. 123, 1925) it is recommended that the conducting medium be called the electrolyte; and that the term "ionogen," suggested by Alexander Smith, be applied to the dissolved substance. This usage will be employed in this book.

(hydrogen) is deposited are the *cathodes*, which are usually designated as minus or negative (−).[2]

The *current density* upon the anode or cathode is the number of amperes per unit area (*e.g.*, per square decimeter or square foot) of the anode or cathode surface. The average current density is computed in any given case by dividing the total current *in any bath* by the total exposed anode or cathode area in the bath. If current is passing to or from both sides of an anode or cathode, the total exposed area should be considered.

Problem.—If in a certain case a current of 25 amp. is passed through a copper solution in which is hung a copper anode 8 × 18 in., and a cathode 12 × 16 in., what are the anode and cathode current densities? The area of the anode is 8 × 18 = 144 sq. in. = 1 sq. ft.; therefore the anode current density is 25 amp./sq. ft. (or $\frac{25}{9.3}$ = 2.7 amp./dm².). The area of the cathode is 12 × 16 = 192 sq. in. = $\frac{192}{144}$ = 1.33 sq. ft.; therefore the cathode current density is $\frac{25}{1.33}$ = 18.8 amp./sq. ft. (or $\frac{18.8}{9.3}$ = 2.02 amp./dm.²).

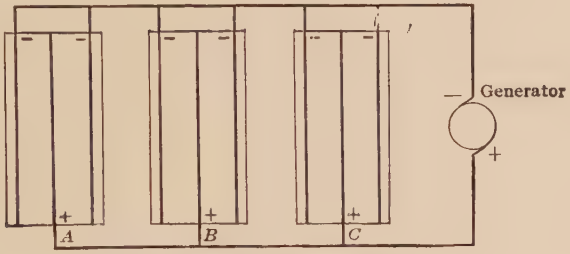


FIG. 2.—Parallel Arrangement of Tanks.

A number of baths operated from one source of current, such as a generator, may be arranged either in parallel or in series. In the **parallel** (or multiple) arrangement, illustrated in Fig. 2, all of the anodes are connected directly to one terminal of the generator, and all of the cathodes to the other terminal. With such an arrangement a current may be passed through any one of the tanks, independently of the others. Disregarding the resistance of the busbars, and assuming that the voltage at the

[1] It is unfortunate that confusion has arisen from the fact that in electrolysis the anode is usually called the positive pole; while in primary batteries it is called the negative pole. To reduce confusion it may be preferable to avoid the use of the terms negative and positive in referring to electrodes, and to call them simply anodes and cathodes.

generator is maintained constant, the current that will pass through each bath will depend upon its resistance, in accordance with Ohm's law. Thus if, in Fig. 2, tank A has a total resistance of 0.01 ohm, B of 0.02 ohm, and C of 0.03 ohm, and an e.m.f. of 6 volts is maintained on the busbars, the current flowing through each tank will be as follows:

$$\text{A} \quad \frac{6 \text{ volts}}{0.01 \text{ ohm}} = 600 \text{ amp.}$$

$$\text{B} \quad \frac{6 \text{ volts}}{0.02 \text{ ohm}} = 300 \text{ amp.}$$

$$\text{C} \quad \frac{6 \text{ volts}}{0.03 \text{ ohm}} = 200 \text{ amp.}$$

and the total current drawn from the generator will be 600 + 300 + 200 amp. = 1,100 amp. If in each tank the cathode area is 20 sq. ft., the cathode current densities will be respectively: (A), $\frac{600}{20}$ = 30 amp./sq. ft.; (B), $\frac{300}{20}$ = 15 amp./sq. ft.; (C), $\frac{200}{20}$ = 10 amp./sq. ft.

If the tanks are arranged in *series*, as shown in Fig. 3, the anodes in one tank are connected with the cathodes in the next

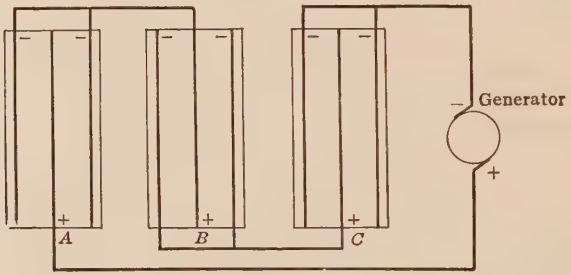


Fig. 3.—Series Arrangement of Tanks.

tank; and only the cathode of the first tank and the anode of the last tank are connected to the generator. With such an arrangement, no current can pass through any of the tanks unless they are all connected as shown, and anodes and cathodes are suspended in each. In a series arrangement, the same total current passes through all of the tanks. The current that passes with a given e.m.f. is determined by the sum of the resistances of the three tanks. Assuming that an e.m.f. of 6 volts is applied, and the tanks have the same resistances as the three previously

discussed, *viz.*, 0.01, 0.02, ant wnd 0.03 ohm, the curreill be

$$\frac{6 \text{ volts}}{0.01 + 0.02 + 0.03 \text{ ohm}} = \frac{6 \text{ volts}}{0.06 \text{ ohm}} = 100 \text{ amp.}$$

which current passes through each one of the three tanks in series. If, as before, the cathode area in each tank is 20 sq. ft., the cathode current density in *each tank* will be equal, *i.e.*, $\frac{100}{20} = 5$ amp./sq. ft. If, however, the cathode area in *A* is 20 sq. ft.; in B, 10 sq. ft.; and in C, 5 sq. ft.; the cathode current densities will be (A), $\frac{100}{20} = 5$ amp./sq.ft.; (B), $\frac{100}{10} = 10$ amp./sq. ft.; and (C), $\frac{100}{5} = 20$ amp./sq. ft. In the latter case, even though the same total current passes through each tank, the current densities, and therefore the rates of deposition, are different in the three tanks. This latter relation is important, showing that in order to get the same current density or rate of deposition in two or more tanks in series, the cathode areas must be equal.

From Ohm's law it follows that in a series arrangement the voltage or potential drop across each tank is proportional to the resistance of the tank. Thus, in the above illustration, the total voltage or potential drop across the three tanks is 6 volts, which is divided in the proportion of the three resistances. Therefore in A the drop is $\frac{0.01}{0.06} \times 6 = 1$ volt; in B, $\frac{0.02}{0.06} \times 6 = 2$ volts; and in C, $\frac{0.03}{0.06} \times 6 = 3$ volts. If in two or more tanks in series, the voltage drop is different, thus if with 5 volts at the generator the drop on one tank is 2 volts, and on the second is 3 volts, the resistances of the two tanks are not equal, which difference may be due to unequal cathode areas or distances, or to a variation in the composition or temperature of the solutions in the two tanks.

CHAPTER VI

PRINCIPLES OF ELECTROCHEMISTRY

Substances which conduct the current are usually divided into "conductors of the first class" and "conductors of the second class." The former comprise those materials, such as the metals, in which the passage of a current causes no chemical change, *i.e.*, no new substances are produced. Conductors of the second class include solutions and molten compounds, which by the passage of a current, *i.e.*, by electrolysis, are decomposed, or at least are changed chemically, with the formation of new substances.

1. FARADAY'S LAW

The fundamental principle underlying electrolysis is known as *Faraday's law*, which may be expressed in the following statements.[1]

(*a*) *The quantity of any element* (*or radical, i.e., group of elements*) *liberated at either the anode or cathode during electrolysis is proportional to the quantity of electricity that passes through the solution.*

(*b*) *The quantities of different elements* (*or radicals*) *liberated by the same quantity of electricity are proportional to their equivalent weights.*

If, for example, under given conditions a coulomb (an ampere-second) deposits 1.118 mg. of silver, then 10 coulombs will deposit $10 \times 1.118 = 11.18$ mg. of silver. It is immaterial whether this total quantity of electricity is produced by the flow of 1 amp.

[1] In certain electrolyses, oxidation may occur at the anode, or reduction at the cathode, without the liberation of any substances upon the electrodes. It is possible to include all such cases if we restate Faraday's law to refer to the total change of valence at the anode or cathode. Such a form of statement includes metal deposition, in which the metal is in every case reduced from its valence in solution to a valence of zero, possessed by all free elements. Since, however, in electrodeposition we are chiefly concerned with the liberation of metals, the historical form of the law is adequate, and will usually be employed.

for 10 seconds or of 2 amp. for 5 seconds, or of any other current for a corresponding period.

The atomic weight of silver is 108, and its valence is one; therefore the equivalent weight of silver is 108. The atomic weight of zinc is 65.4 and its valence is two; hence the equivalent weight of zinc is $\frac{65.4}{2} = 32.7$. If, therefore, one coulomb deposits 1.118 mg. of silver, it will deposit $\frac{32.7}{108} \times 1.118 = 0.339$ mg. of zinc. This relation between the weights of metals liberated by a given current can be illustrated by passing a current through a number of solutions connected (electrically) in series, and containing suitable solutions of various metals, such as silver nitrate, copper sulphate, nickel sulphate, lead fluoborate, etc. The maximum quantities of the various metals deposited will then be in the proportion of their equivalent weights (the atomic weights divided by the valences), *viz.*, Ag, 108; Cu^{+II}, 31.8; Ni, 29.3; and Pb, 103.5.

To deposit the equivalent weight *in grams* of silver, *i.e.*, 108 g., will require the passage of $\frac{108}{0.001118} = 96{,}500$ coulombs. This quantity of electricity, which will also liberate an equivalent weight in grams of any other element, is known as a *faraday.* It is equal to 26.8 amp.-hr., a convenient value to remember in making calculations of the weight of metal that may be deposited by a certain current in a given time. Thus, *e.g.*, an ampere-day, or 24 amp.-hr., will deposit about 10 per cent less than the equivalent weight in grams of any element.

2. CURRENT EFFICIENCY

Faraday's law defines the total quantity of substances, such as metals, liberated at an electrode by the passage of a certain quantity of electricity, but does not indicate which elements will be discharged at the electrodes under any given conditions. From a zinc sulphate solution it is possible to deposit upon the cathode, under certain conditions, only zinc, while under other conditions (*e.g.*, with an excess of acid, or at high current densities) a large amount of hydrogen may be evolved at the cathode, in which latter case part of the current is consumed in the deposition of hydrogen. Since in electrodeposition the purpose usually is to deposit a certain metal, it is customary to consider,

as the *current efficiency* of the electrolysis, that proportion of the current which is actually used to dissolve or deposit that metal. Thus the *cathode efficiency* may be defined as the ratio of the weight of metal actually deposited by a given current to the maximum weight of that metal which could be deposited according to Faraday's law. In Table 9 (Appendix) it is shown that 1 coulomb will deposit (under ideal conditions) 0.339 mg., or 0.000339 g., of zinc; or 1 amp.-hr. will deposit $3{,}600 \times 0.000339$ g. = 1.22 g. of zinc. If in an actual case the weight of zinc deposited during the passage of 1 amp.-hr. was found to be 1.17 g., the cathode efficiency would be $\frac{1.17}{1.22} = 0.96$, or 96 per cent.

Similarly, the *anode efficiency* is the ratio of the weight of metal dissolved from the anode to the maximum weight of metal that could be dissolved according to Faraday's law, by the quantity of electricity passed through the solution. It is important to remember that the current efficiency at both the anode and cathode is always 100 per cent, with respect to the *sum of the products of electrolysis* (or, more strictly speaking, with respect to the total changes in valence). Thus in a brass plating solution, the sum of the amounts of copper, zinc, and hydrogen liberated at the cathode is equivalent to the current passed through the solution, even though the *metal* cathode efficiency may be low.

To determine the cathode efficiency in any given operation, it is merely necessary to weigh carefully the cathode before and after the passage of a definite quantity of electricity. The quantity of electricity that passes may be roughly estimated from the average current as indicated by an ammeter and the period of deposition. If, for example, a current of 12 amp. is passed through a solution for 2 hr., the total quantity of electricity is equal to 24 amp.-hr. This method of measurement is, however, subject to error, due to possible variation of the current at different periods during the deposition, and to possible errors in the ammeter calibration and in measuring the time. For reliable results it is therefore necessary to measure the current by placing in the circuit an electrolytic bath, known to have a cathode efficiency of 100 per cent (or practically 100 per cent). Such a bath is known as a *coulometer* (or *voltameter*). For very accurate measurements a silver coulometer is employed (page 54), but for all practical purposes a copper coulometer is sufficiently

accurate. Such a coulometer consists simply of an acid copper bath of suitable size, in which are hung a copper anode and a weighed copper cathode. A solution containing 150 g./l. (20 oz./gal.) of copper sulphate, and 60 g./l. (8 oz./gal.) of sulphuric acid, or, in fact, any good acid copper bath, may be used in the coulometer to secure an accuracy within about 1 per cent. (The addition of a small amount of ethyl alcohol to the bath makes the results more accurate, but this is usually not necessary.) The cathode should be of such a size that the current density upon it will not exceed about 1 amp./dm.^{2} (9.3 amp./sq. ft.) or be less than 0.1 amp./dm.^{2} (0.93 amp./sq. ft.). If such a bath is connected in series with one or more baths of which it is desired to test the current efficiency, the same current necessarily flows through all the baths for the same length of time. If, therefore, the weight of the deposited copper is determined, the total number of coulombs may be calculated, and by reference to Table 9 (in the Appendix), the maximum weight of any other metal that could be deposited by that current can be computed. By comparing with this weight the actual weights of metals deposited, the cathode efficiencies can be determined.

Problem.—Suppose that a certain current is passed through three baths in series, *viz.*, (*a*) an acid copper bath as described above, (*b*) a nickel bath, and (*c*) a zinc bath; and the weights of the metals deposited upon the cathodes are: (*a*) 35.6 g. of copper, (*b*) 29.2 g. of nickel, and (*c*) 34.8 g. of zinc. What are the cathode efficiencies of the nickel and zinc baths?

According to Table 9, 1 amp.-hr. deposits 1.186 g. of copper; therefore (assuming 100 per cent efficiency for the copper coulometer) the quantity of electricity passed $= \frac{3.56}{1.186} = 30$ amp.-hr. 30 amp.-hr. will deposit a maximum of $30 \times 1.095 = 32.8$ g. of nickel; if, therefore, only 29.2 g. were deposited, the cathode efficiency was $\frac{29.2}{32.8} = 0.89$, or 89 per cent. Similarly, 30 amp.-hr. will deposit a maximum of $30 \times 1.22 = 36.6$ g. of zinc; and if only 34.8 g. were deposited, the cathode efficiency was $\frac{34.8}{36.6} = 0.95$, or 95 per cent.

The anode efficiencies can theoretically be calculated in exactly the same way, by comparing the loss in weight of the anode with the *increase in weight of the copper cathode* in the copper coulometer (which is considered as 100 per cent). It is difficult to measure anode efficiencies, owing to the fact that particles of undissolved metal, or of impurities, almost invariably drop from the anodes and hence render the weights uncertain. The best

practical method of estimating the relative anode efficiency is to determine whether the metal content of the solution changes. If it stays constant, the anode efficiency must be equal to the cathode efficiency; and if it increases, the anode efficiency is higher than the cathode efficiency by an amount which can be calculated from the increased metal content, the volume of the solution, and the total current passed. If the metal content decreases, the anode efficiency is lower than the cathode efficiency by a corresponding amount.

The total loss in weight of metal from an anode during electrolysis may consist of three parts; (*a*) the metal that has actually passed into solution, (*b*) metal that has been acted on to form compounds which are insoluble or very slowly soluble in the solution and (*c*) metallic particles that have become detached from the anode without being chemically changed. Of these (*a*) is the only useful product of the electrolysis, and therefore is the only true basis for estimating the anode efficiency.

It is still more difficult to express the anode efficiency of an alloy such as brass. A convenient, though arbitrary way of doing so, is to base it upon the amount of the two metals that would be dissolved if the current were divided in proportion to the chemical equivalents of each metal present in the alloy, and if each passed into solution with 100 per cent efficiency. An illustration of this principle will be given under brass plating (p. 382).

Difficulty is experienced in making any reliable measurements of anode efficiency on a commercial scale because some of the solution is lost by "*drag-out*," *i.e.*, it adheres to the cathodes when they are removed from the plating bath, and is lost in rinsing. It is not possible to measure directly the volume of solution lost by drag-out, because (*a*) water is continually evaporating from the baths, (*b*) water is introduced with the wet articles that are hung in the baths, and (*c*) even if these errors could be reduced it would be impractical to measure a difference of as little as 1 per cent in the depth of the solution. A loss of 1 per cent per day would represent a very large drag-out.

The drag-out can be calculated indirectly from the changes in concentration of any constituent of the bath that is not deposited or removed from the bath in any way except by drag-out. Thus in a nickel bath containing magnesium sulphate, it may be safely assumed that no magnesium is deposited or carried into

the sludge. Suppose for example that a 1,000 gal. bath contained at the beginning of a run, magnesium equivalent to 4 oz./gal. or 4,000 oz. in all of magnesium sulphate; and during a run of 50 days 100 lbs. or 1,600 oz. of magnesium sulphate was added. If at the end of the run it was found that the solution contained 4.6 oz./gal. or a total of 4,600 oz. of magnesium sulphate, it is evident that out of the 4,000 + 1,600 = 5,600 ounces originally present or added, only 4,600 oz. remain. Hence 5,600 − 4,600 = 1,000 oz. of magnesium sulphate was lost in the drag-out. The average concentration of magnesium sulphate during the entire period was $\frac{4.0 + 4.6}{2} = 4.3$ oz./gal. Therefore $\frac{1{,}000}{4.3} = 232$ gal. of the solution was lost in 50 days. This is equivalent to $\frac{232}{1{,}000} = 23.2$ per cent. Therefore the average daily loss was $\frac{23.2}{50} = 0.46$ per cent. In other words a volume equal to the total volume of the plating tank would be thus removed in $\frac{100}{0.46} = 218$ days.

The actual magnitude of the drag-out from any bath varies greatly with the shape of the pieces plated, and the number that pass through in a given time, which in turn depends on the length of time they are plated. The loss may be very great if the articles tend to hold plating solution, and if they are plated for only a short time, *e.g.*, 10 min. or less. Thus C. F. Nixon,[1] in one of the very few papers that deals with this subject, found by calculations similar to the above but based on chloride and boric acid, a loss of 980 gal. of solution in 504 working hours, from a mechanically operated tank containing 1,346 gal. This is equivalent to a "drag-out number" as defined by Nixon of 3.2, *i.e.*, the solution would be renewed 3.2 times in a working year. (In the previous example the drag-out number would be, on the basis of 300 working days, 1.38.)

It is highly desirable that more measurements of this sort should be made in different plants. If figures such as those of Nixon are confirmed under other conditions, it indicates that the loss of chemicals through drag-out may not be negligible, and that even with nickel baths, steps should be taken to recover a

[1] *Monthly Rev., Am. Electroplaters' Soc.*, Vol. 15, March, 1928.

part of the metal. Such steps are now commonly used in silver and gold plating, and occasionally in chromium plating. In such measurements it is necessary to show that no significant amount of the constituent considered enters into the sludge. It is possible in nickel baths that sulphate, chloride, and boric acid may enter the sludge, and thus cause an erroneously high value for drag-out.

The economic losses caused by drag-out depend, not on the volume of solution removed, but on the concentration and cost of the constituents. Even dilute solutions of silver and gold represent large monetary losses. When a strong solution such as 420 g./l. (56 oz./gal.) of chromic acid is used, the daily losses may also be considerable, especially if the articles are plated for only a few minutes. The practical way to reduce drag-out losses, is to employ a drip tank, followed by a "standing rinse" tank, the water from which is used to replace the water evaporated from the tanks. If this evaporation loss is insufficient to utilize the first rinse water the latter may be concentrated by evaporation, or the valuable constituents, such as silver or gold, may be recovered from it by chemical precipitation.

3. ELECTRODE POTENTIALS

In considering the effects of an electrical current, it is necessary to take into account both the *quantity* factor and the *intensity* factor, which are measured respectively by the number of amperes (or coulombs in a given period), and by the e.m.f., or number of volts required in any circuit or part of a circuit to cause the electricity to flow at such a rate. Faraday's law refers only to the quantity of any substance that may be liberated by a certain current, and gives no indication of the voltage required. As shown on page 55, however, the voltage employed to produce a given current determines the power required to conduct the process.

The simplest and most commonly used method of electrodeposition consists in the electrolysis of a suitable solution containing the metal to be deposited, with an anode consisting of that same metal and (after deposition has commenced) a cathode covered with that metal. Let us consider the operation of an acid copper bath as a simple illustration. If between the electrodes in such a bath, a definite e.m.f. or voltage is maintained by means of a battery or generator, a current will pass

continuously through the solution. The magnitude of this current will depend upon the resistance of the bath and upon the applied e.m.f., in accordance with Ohm's law. Thus, if the resistance of the bath is 0.03 ohms; and an e.m.f., of 6 volts is applied,

$$I = \frac{E}{R} = \frac{6}{0.03} = 200 \text{ amp.}$$

If 1 volt is applied,

$$I = \frac{1}{0.03} = 33 \text{ amp.}$$

If only 0.1 volt is employed,

$$I = \frac{0.1}{0.03} = 3.3 \text{ amp.}$$

In other words (assuming for the sake of illustration that such a copper bath represents an "ideal" bath), a certain though small current will flow through the solution if any potential difference, however small, is maintained between the anode and cathode. For this ideal case, then, it may be stated that: (*a*) To cause a current to pass through a solution, no minimum potential difference is required, and (*b*) the current that passes corresponds to Ohm's law.

The above conditions are approximately fulfilled only if there is no appreciable "*polarization*" at either the anode or cathode. By polarization is meant the change in potential at the actual electrode surface, that occurs as a result of passing the current. Before discussing this polarization, it is necessary to consider what is meant by the electrode potentials, or the single potentials of metals.

When any metal is dipped into a solution of one of its salts containing ions of that metal there is a certain tendency for the metal to go into solution and to form positively charged ions of the metal. In other words, there is a certain "solution pressure" of the metal. On the other hand, the metal ions in the solution exert a certain pressure ("osmotic pressure") which tends to oppose or counteract this solution pressure of the metal. The relation between the solution pressure and the osmotic pressure of the ions is expressed in terms of the *potential difference* between the metal and its solution. In order to measure and compare these potential differences, it is necessary to select some potential

difference which is arbitrarily called the *zero potential difference,* or to which some definite value is assigned (with respect to some other standard of reference). Thus, in order to measure the potential difference between copper and a solution of copper sulphate, such a combination must be suitably connected to another electrode immersed in a definite solution, and of which the potential difference is known. The common working standard of comparison is the *normal calomel half cell,* which consists of a mixture of mercury and mercurous chloride immersed in a normal solution of potassium chloride. The accepted zero of potential difference is that of a hydrogen electrode (page 101) immersed in a solution in which the hydrogen ion concentration is normal. With respect to this zero potential, the potential of the calomel half cell is + 0.283 volts. (The normal hydrogen electrode and the calomel half cell bear a relation to each other and to any other electrode potentials similar to that which a mark at sea level, and a "bench mark" of known elevation above sea level, bear to the measurement of relative levels or elevations in surveying.) As thus measured, the potentials of any metals with respect to their solutions are spoken of as the "single potentials" of those metals. Necessarily these potentials will vary with the concentration of the ions of that metal in the solution. In general, the greater the concentration of the metal ions, the less will be the tendency to dissolve, and vice versa. It is obvious that zinc will have a smaller tendency to pass into a solution which contains a large concentration of zinc ions than into one which contains a small number of zinc ions; just as a salt will dissolve less readily in a concentrated solution than in one which contains only a small amount of that salt. In order to permit a proper comparison of the relative solution pressures of different metals, their single potential differences are usually expressed with respect to solutions (in most cases hypothetical) in which the metal ion concentration is normal.

If the metals are arranged in the order of the normal potentials of the reactions by which they form ions, the so-called *electromotive series* is obtained. Such a series, arranged with respect to hydrogen as zero, is illustrated for the common metals in Table 10 in the Appendix. It should be noted that all of the metals above hydrogen in this list are capable of displacing hydrogen from solutions containing hydrogen ions, in other words, are soluble in acids, and those below

hydrogen are usually unable to displace hydrogen directly. Similarly, if any metal in this series, in contact with its solution, is connected with a metal and solution lower in the series, a primary battery is produced, of which the electromotive force is equal (approximately) to the algebraic difference between the two potentials. Thus if a cell were constructed with zinc in a zinc solution of normal zinc ion concentration,[1] and silver in a silver solution of normal silver ion concentration, an e.m.f. of approximately 1.56 volts (the algebraic difference between − 0.76 and + 0.80) would be produced. As a result of the reaction in such a battery, the metal higher in the series (in this case zinc) always goes into solution, and the lower metal (silver) is precipitated from its solution. In other words, each metal is capable of displacing from its simple solutions any metal lower in the series. This is often designated as "deposition by immersion." It is important to bear in mind, however, that this order is true only for simple solutions of approximately equal metal ion concentrations; and that if the latter are materially changed, as, *e.g.*, by the formation of complex ions, as in the cyanide solutions, the values and even the order of the potentials may be changed.

4. SIGN OF POTENTIALS

In Table 10, the "base" metals such as zinc, tin, and lead, which most readily dissolve in acids, are represented as having a negative potential, and the "noble" metals such as copper, silver and gold, as having a positive potential. This usage, which has been adopted by many technical societies and by the Bureau of Standards, is exactly the opposite of that formerly employed and still found in some texts. It is not necessary here to discuss the reasons which led to this change.[2] It is important, however, to note this difference and to avoid confusion. In the

[1] A solution with "normal ion concentration," is one containing in each liter one equivalent in grams of the ion specified. Thus a solution with normal zinc ion concentration would contain, not 32.5 g./l. of *zinc*, but of *zinc ions;* and one of silver would contain 108 g./l. of silver ions. Actually such concentrated solutions cannot usually exist and therefore the normal potentials are computed from measurements in more dilute solutions, in which the metal ion concentrations are measured or assumed. The normal potentials are therefore usually calculated and not measured values.

[2] A discussion of these reasons will be found in *Trans. Am. Electrochem. Soc.*, vol. 36, pp. 3–15, 1919.

system used in this book, a more negative potential indicates a greater tendency for the metal to pass into solution and vice-versa.

The use of the positive sign for the potential of zinc has been so common in chemical and electrochemical texts that for some time there will be uncertainty, even if the negative sign is universally adopted. One of the most probable sources of confusion is the common reference to zinc as being more positive than iron, and therefore protecting the iron from corrosion. It is suggested that such uncertainty may be avoided by referring to the zinc not as being more positive or negative than the iron, but as having a greater solution pressure, *i.e.* a greater tendency to dissolve, than the iron. The same conception is involved in the reference to zinc and other metals which stand above hydrogen in the series as the "base" metals, and to copper and the metals which stand below hydrogen as the "noble" metals. A definite meaning is conveyed by the statement that zinc is more "base" than lead, or that gold is more "noble" than copper.

For the exact measurement of electrode potentials, or, more strictly, of the potential difference produced by a combination of two electrodes, a *potentiometer* is used. The principle of a potentiometer is that the unknown e.m.f. is balanced against an adjustable and measurable e.m.f., so that when no current flows (as indicated by a galvanometer or a capillary electrometer) it is established that the e.m.f. to be measured is numerically equal, but of opposite sign to, the known potential. The equipment and manipulation required are such that no reliable measurements of potentials can be made by one not familiar with such methods.

5. POLARIZATION

When a direct current is passed through a copper sulphate solution between two copper electrodes, copper dissolves from the anode, and deposits upon the cathode. It is obvious that in this process there is a tendency for the solution at the surface of the electrodes to change in concentration. At the anode the solution tends to become stronger, because copper has there passed into the solution, while at the cathode it tends to become weaker because the copper has there been removed from the solution. If the solution at the anode becomes stronger, there is less tendency for copper to dissolve, hence it requires an

increased potential or voltage to continue the passage of the current. Similarly at the cathode it is more difficult to deposit copper from a dilute than from a concentrated solution, and hence a higher voltage is required at the cathode. This increase in voltage at the electrodes above that necessary to make the process start, is called the polarization, which may be divided into anode polarization and cathode polarization.

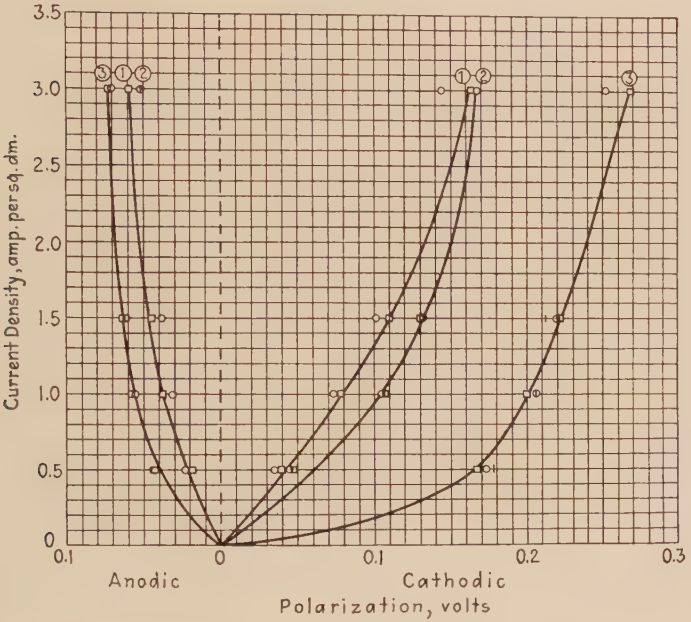


FIG. 4.—Polarization Curves in Copper Deposition.
Curve:
1—Solution A, 1.5 *N* $CuSO_4$, 1.5 *N* H_2SO_4.
2—Solution A + 0.002 g./L. glue.
3—Solution A + 0.02 g./L. glue.

The existence and magnitude of this polarization at each electrode is indicated by the fact that as the current density is increased the potential of the anode always becomes more positive, and that of the cathode becomes more negative. This is illustrated for typical copper solutions in Fig. 4, in which the curves at the left show the anode polarization, and at the right, the cathode polarization.

Another evidence of polarization is the fact that if the circuit is suddenly broken, a potential or voltage will still exist between

the anode and cathode, but opposite in direction. This is because the polarization sets up a counter e.m.f., which opposes the passage of the current, and hence requires the application of a higher voltage to produce a given current than if there were no polarization. It is not possible to measure the polarization accurately from this voltmeter reading, because it falls off too rapidly.

A simple method of measuring polarization[1] that has given approximate results in copper and nickel solutions, depends upon

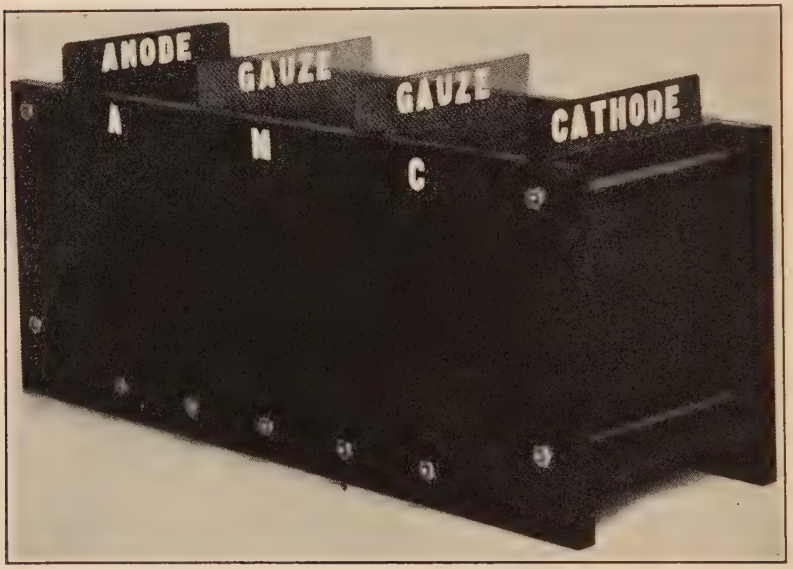


FIG. 5.—"Haring Cell" Developed for Polarization and Resistivity Measurements.

the fact that in any electroplating bath with a soluble anode, the total voltage required is equal to the sum of (*a*) the voltage needed to overcome resistance, known as the *IR* drop (p. 54), (*b*) the anode polarization, and (*c*) the cathode polarization.

The "polarization box" shown in Fig. 5 is divided into three equal parts by two wire gauzes placed between the anode and cathode. If instead of wire gauzes, solid plates were inserted, metal would deposit on one side of each plate and dissolve from the other side, just as in series copper refining. Hence there

[1] HARING, H. E., *Trans. Am. Electrochem. Soc.*, vol. 49, p. 417, 1926.

would be anode polarization on one side and cathode polarization on the other side of each plate. But with the gauzes, the solutions on the two sides mix and there is no polarization on the gauzes. Hence the voltage between the two gauzes is due entirely to the *IR* drop, and may be used to measure the resistivity (p. 71) of the solution. But in the anode compartment of equal length there must be an equal *IR* drop plus the anode polarization; and in the cathode compartment an equal *IR* drop plus the cathode polarization.

To measure these polarizations for a given current density all that is necessary is to pass the appropriate current and to measure with a potentiometer or a high resistance voltmeter, the total voltage in each compartment. Suppose a current of 0.25 amp. is passed between electrodes having an exposed area of 5 × 5 cm. (2″ × 2″), *i.e.*, 25 cm.^{2} or 0.25 dm.^{2} (or 4 sq. in.). Then the current density is 1.0 amp./dm.^{2} or 9.3 amp./sq. ft. If the respective voltages are

	Volts
Anode section	1.15
Middle section	0.95
Cathode section	1.25

Then

Anode polarization = 1.15 − 0.95 = 0.20 volt and
Cathode polarization = 1.25 − 0.95 = 0.30 volt.

By making a series of such measurements at different current densities, polarization curves such as shown in Fig. 4, p. 71 may be constructed. As will be shown later, cathode polarization curves are useful in predicting the throwing power and other properties of the solutions. They are seldom of interest in themselves.

Whenever the anode polarization is very high, the anode dissolves with difficulty or not at all, and is said to be *passive*. Passivity of anodes often occurs in plating, *e.g.*, with pure nickel anodes in solutions containing little or no chloride; or copper anodes in a cyanide solution containing insufficient free cyanide. The passivity may be accompanied (or caused) by a visible accumulation of insoluble products on the anode, or it may be due to an invisible film of oxide or other compounds.

When gases are discharged, *e.g.*, oxygen on the anode, or hydrogen on the cathode, there is usually a considerable polar-

ization, which is commonly referred to as "*overvoltage.*" This overvoltage differs with the composition and surface condition of the electrodes, and with the current density. Its practical importance in electroplating lies in the fact that if it were not for the hydrogen overvoltage, it would not be possible to plate metals such as zinc from acid solutions. Except for the presence of hydrogen overvoltage, we would expect hydrogen to deposit on the cathode at a much lower voltage than zinc.

Just as with other types of polarization the overvoltage of hydrogen or of oxygen depends upon the composition and surface condition of the electrodes, the composition and temperature of the solution, the current density employed, and the method of measurement. It is not possible therefore to state a definite *value* for the overvoltage of hydrogen or oxygen on a given metal. Tables (such as Table 13 Appendix) showing the *relative* overvoltages on different metals are useful as a guide though even the order may be changed by a variation in conditions.

6. RESISTANCE

In the preceding discussion we have considered principally the e.m.f. or driving force which makes possible the flow of current through any solution, and the factors which oppose or counteract it. From Ohm's law it is evident, however, that the magnitude of the current that passes through any circuit is determined not only by the e.m.f. applied but also by the resistance of the bath.

The total *resistance* of any plating unit is determined by (*a*) the size, shape, and electrical conductivity of the electrodes; and (*b*) the resistance of the portion of solution or electrolyte between the electrodes. Since most of the metals used either as anodes or cathodes are relatively good conductors, the actual resistance of the electrodes is usually small compared with that of the solution. The principal reason that the current flowing is increased by increasing the size of the electrodes is not because of the lower resistance of the larger electrodes, but because a larger portion of the solution thereby becomes effective in conducting the current. We are therefore concerned principally with the resistance of the solution.

The actual resistance (in ohms) of a definite portion of a plating solution in a tank depends upon its shape and size and

upon the *resistivity* of the particular solution, which in turn depends upon its composition and temperature. Although the terms are frequently used interchangeably, it is essential to distinguish between the *resistance* of a certain bath and the *resistivity* of the solution in the bath. Thus a particular copper bath, containing a certain solution and with certain electrodes in it, may have a *resistance* of 0.03 ohm, but the solution present in it may have a *resistivity* of 5 ohm-cm. (or ohms per centimeter cube). Similarly, it is important to understand the relation of the terms *resistivity* and *conductivity*, and of the terms *resistance* and *conductance*, which terms in each pair, represent "reciprocal" properties. Thus if solution A has a resistivity twice as great as that of B, then A must have only one-half the conductivity of B. If the resistivity of a solution is 5 ohm-cm., its conductivity must be 1/5 (or 0.2) reciprocal ohm-cm. or "mho-cm." Similarly, if a tank has a resistance of 0.02 ohm, it has a conductance of 50 reciprocal ohms or "mhos." In many electrochemical calculations the values for conductivity are useful, but in commercial electrodeposition it is far simpler to compare directly the resistivities of the solutions, especially as in the customary units these are usually expressed in numbers greater than one, while conductivities are expressed in fractions or decimals. Thus it is easier to gain a conception of the relative usefulness of two nickel solutions from the statement that their specific resistivities are respectively 18 and 24 ohm-cm. than from the equally correct statement that their specific conductivities are 0.056 and 0.042 reciprocal ohm-cm. Another advantage in expressing the resistivities is that in the so-called measurement of conductivity, the property measured directly is a resistance, which can be more simply converted to a resistivity than to a conductivity.

The specific resistivity is usually measured in "ohms per centimeter cube," *i.e.*, the resistance of a portion of the solution having a cross-section of 1 sq. cm. and a length of 1 cm. The unit for expressing such values is the "ohm-centimeter." It is of course possible to compare the resistivities of solutions in terms of other volumes, such as "1-in. cube," or, as has been suggested by some writers on electroplating, a unit volume 1 sq. in. in cross-section and 6 in. long may be employed. The resistivity per inch cube is 0.39 (or practically 0.4) times that of a centimeter cube; and for a volume 1 sq. in. in cross-section and

6 in. long, the resistivity is 2.36 that of a centimeter cube. As, however, the relative and not the absolute values are usually of interest, it is far preferable for those who desire to compare the resistivities of certain solutions to become accustomed to the values in terms of ohm-centimeters, *i.e.*, of ohms per centimeter cube, such as are given in Table 11, in the Appendix. (These are numerically equal to the resistance of a portion of solution 1 sq. in. in cross-section and 2.54 in. long.)

Measurement of Resistivity.—The simplest way to measure the resistivity of a solution would be to apply a definite e.m.f. between two electrodes of definite and equal size and measure the current which passes between them. In order to have between the electrodes a defined column of liquid, it is necessary for the electrodes to fill entirely the cross-section of the vessel in which the solution is placed. Suppose that in such a case two copper electrodes each 10 × 10 cm. (4 × 4 in.) were placed in a box of that same cross-section at a distance of 10 cm. (4 in.) apart, and were just covered with a sample of an acid copper bath to be tested. If when the electrodes were connected with a storage battery, an ammeter, and a voltmeter, it was found that the potential difference between the electrodes was 2 volts, and a current of 3 amp. was flowing, what would be the resistivity of the solution? Since

$$R = \frac{E}{I}, \quad R = \frac{2}{3} = 0.67 \text{ ohm} =$$

the resistance of that portion of solution between the electrodes (neglecting that of the electrodes themselves). Since, however, the distance between the electrodes was 10 cm., the resistance of a column 1 cm. long would have been correspondingly less; therefore $\frac{0.67}{10} = 0.067$ ohm, which is the resistance of a column of the solution 100 cm.^{2} (10 = 10 cm.) in cross-section, and 1 cm. thick. The resistance per centimeter cube would, however, be 100 times as great, or 100 × 0.067 = 6.7 ohm-cm., or ohms per centimeter cube. Making the same calculations in ordinary units, the resistance for 1-in. thickness of solution would have been $\frac{0.67}{4} = 0.168$ ohm; and for 1-in. cube, 0.168 × 16 (or 4 × 4) = 2.69 ohm per inch cube.

If however attempts were made to measure the resistivity of a solution in such a box with two plane parallel electrodes, it would be found that the voltage did not increase proportionally with the current, in accordance with Ohm's law. Consequently a different value for the resistivity would be obtained depending upon the current used. This is because of the fact (p. 72) that in addition to the resistance, the voltage used must overcome the anode and cathode polarization. When intermediate gauze electrodes are used, as shown in the Haring cell (p. 72), there is no polarization on the gauzes, and the voltage between them is due entirely to the resistance. This furnishes a simple method for measuring resistivity with an accuracy of about 1 per cent, which is fully adequate for most experiments in plating.

The data on p. 73 may be used to illustrate the calculation of resistivity. In the middle section, which was $5 \times 5 \times 5$ cm. (2 in. $\times$ 2 in. $\times$ 2 in.) the voltage drop was 0.95 volts, when a current of 0.25 amp. was passed. Then

$$R(\text{the resistance of the center section}) = \frac{E}{I} = \frac{0.95}{0.25} = 3.8 \text{ ohms.}$$

Then the *resistivity* of the solution

$$r = \frac{R \times l\,(\text{length}) \times w(\text{width})}{d(\text{distance})} = \frac{3.8 \times 5 \times 5}{5} = 19 \text{ ohm-cm.}$$

For a box of these dimensions, the resistivity of the solution used is equal to five times the ratio of the voltage in the center section to the current.

In order to overcome the effects of polarization in more accurate conductivity measurements, an alternating current is used, since by the alternation the products causing polarization are removed as soon as formed. For work of high precision, high-frequency, low-voltage currents are used, but for ordinary accuracy, the regular 60-cycle, 110-volt, a.c. lighting current may be employed. Simple apparatus for making such conductivity measurements is now available. The principle of all such apparatus is that of the Wheatstone bridge, in which the unknown resistance is determined by comparing it with known resistances. Diagrammatically the connections are illustrated in Fig. 6. If by means of a suitable battery E, a definite e.m.f. is maintained between the points F and H, part of the current will pass through the shunt FIH, and part through the shunt FKH. If, now, a point I on one branch is connected through a galvanometer,

G, to a point K on the other branch, and the resistances are so adjusted that no current flows from I to K, shown by the needle of the galvanometer remaining stationary, then the resistances in the two parts of each branch are proportional; in other words, $\frac{A}{B} = \frac{C}{D}$. If the unknown resistance is placed in the branch A, then its resistance is readily calculated, as $A = \frac{BC}{D}$.

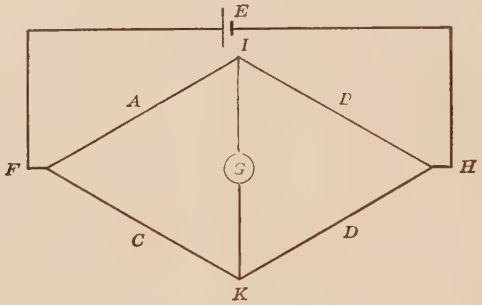


Fig. 6.—Diagram of Wheatstone Bridge.

In measuring conductivities an alternating current is used, for the reasons explained above, and hence a d.c. galvanometer cannot be employed. For making accurate conductivity measurements a sensitive telephone receiver is used to determine when the bridge is "balanced," that is, when the resistance of the various arms are so adjusted that no current flows between the points corresponding to I and K. For low-frequency alternating current, which can be used for approximate conductivity measurements, an a.c. galvanometer may be used. In apparatus now available, which is designed especially for commercial measurements, such a galvanometer is mounted in the box with the bridge.

In making conductivity measurements, a cell with platinum electrodes which are coated with platinum black should be employed. A form of cell which has proved convenient for approximate conductivity measurements is shown in Fig. 7. This has been designed especially to facilitate cleaning and filling.

Such a cell should be kept at nearly a constant temperature during the measurements, *e.g.*, by immersion in a large bath maintained at a constant temperature, since a change of 1°C.

(1.8°F.) produces a change of about 2 per cent in the conductivity of aqueous solutions. It is not necessary that the cell should have any exact dimensions, as the "cell constant" must in any case be determined. This is accomplished by placing in the cell a normal potassium chloride (KCl) solution, of which the specific resistivity at 25°C. (77°F.) is 8.94 ohm-cm. If for a certain cell the resistance, when filled with normal KCl, is found

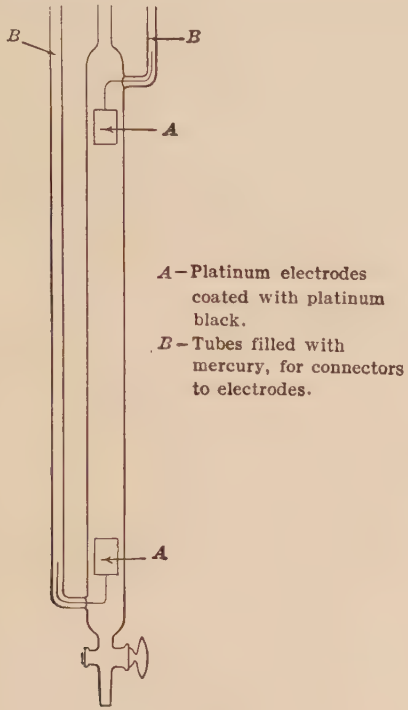


FIG. 7.—Conductivity Cell.

to be 210 ohms, the constant of the cell is $\frac{210}{8.94} = 23.5$. The "cell constant" is the resistance of the cell when filled with a hypothetical solution of unit resistivity, *i.e.*, of 1 ohm-cm. This value is applied in making other measurements in the following way. Suppose that the resistance of the cell when filled with an acid copper solution is 150 ohms. Then the resistivity of the copper solution is

$$\frac{150}{\text{Cell constant}} = \frac{150}{23.5} = 6.4 \text{ ohm-cm.}$$

In Table 11 (Appendix) will be found a list of approximate resistivities of solutions which are used directly or indirectly in electrodeposition. In general it will be observed that the strong acids and alkalis have the lowest resistivity (highest conductivity) and that the salts of the alkali metals (sodium, potassium, and ammonium salts) are next in order. The salts of the heavy metals, *i.e.*, those of copper, silver, zinc, tin, lead, nickel, etc., are not very good conductors; and therefore, whenever possible, acids are added to increase the conductivity (as sulphuric acid in the acid copper bath), or alkali salts are added to neutral solutions (such as sodium sulphate to a nickel bath), or excess alkali is added to alkaline solutions (such as sodium hydroxide to the zinc cyanide bath). Because, as explained on page 22, the presence of ions in a solution is necessary for the passage of a current, it follows that those solutions will conduct best in which the greatest number of ions are present. The strong acids and bases are dissociated to a greater extent than the weaker acids, and are therefore better conductors. Another reason for the greater conductivity of acids and bases is that the hydrogen ions set free from the acid, and the hydroxyl ions set free from the base, have greater *mobilities*, that is, move with higher "migration velocities" than any other ions.

A knowledge of the approximate resistivities of plating solutions and of materials used in their preparation is of practical value in predicting the *relative* voltages required to produce desired current densities, and the relative effects of various possible additions upon the conductivity of the solutions. Thus, for example, if copper solution A has a specific resistivity of 6 ohm-cm., and solution B has a resistivity of 9 ohm-cm., it will require approximately 3 volts in B to produce the same current density as is produced in A with 2 volts. Similarly, if the resistivity of a normal ammonium sulphate, $(NH_4)_2SO_4$, solution (13 ohm-cm.) is less than that of a normal magnesium sulphate ($MgSO_4$) solution (30 ohm-cm.) the addition of ammonium sulphate will produce a greater decrease in resistivity (increase in the conductivity) of a nickel solution than will an equivalent (not equal) amount of magnesium sulphate. Whether the ammonium sulphate is actually more beneficial may depend upon factors other than the conductivity.

It is not possible, however, to calculate with even approximate accuracy the current density that will be produced in a plating

bath of known resistivity by the application of a definite e.m.f. between even two plane parallel electrodes, unless these entirely fill the cross-section of the tank. This condition never exists in practice, and the current passes between the anodes and cathodes, not merely through the solution lying directly between them, but also, to a slight extent at least, through all portions of the solution in the tank. The actual current produced is therefore always greater than would be calculated from the electrode areas, their distance apart, and the resistivity of the solution. This may be illustrated by the following actual observations.

In an acid copper bath 75 cm. (30 in.) wide, and in which the solution was 65 cm. (26 in.) deep, a number of anodes and cathodes each having an area on each side of about 14 dm.^{2} (1.5 sq. ft.) were placed at intervals of 6 cm. (2.4 in.). The solution had a resistivity of 6 ohm-cm., and an e.m.f. of 1 volt was maintained between the anode and cathode. What current density was produced on the cathodes? For a column 1 cm.^{2} in cross-section and 6 cm. long, the resistance would be $6 \times 6 = 36$ ohms. The cathode area was 14 dm^2., or 1,400 cm.^{2}; therefore the resistance of a layer of liquid 6 cm. thick and 1,400 cm.^{2} in cross-section would be $\frac{36}{1{,}400} = 0.026$ ohm. If the applied e.m.f. was 1 volt, we would expect $I = \frac{E}{R} = \frac{1}{0.026} = 38$ amp. As this was on an area of 14 dm.^{2}, the current density would be $\frac{38}{14} = 2.7$ amp.-dm.^{2}, or $2.7 \times 9.3 = 25$ amp./sq. ft. Actually, under these conditions the current density was about 4 amp./dm.^{2}, or 37 amp./sq. ft. showing that about 50 per cent additional current was carried through the solution lying outside of the bounds of the electrodes.

With the irregular-shaped articles which are usually electroplated, it is still less possible to calculate the actual current density from the conductivity, since it is almost impossible to compute either the effective area to be plated, or the average distance between the anodes and cathodes.

Effect of Temperature on Resistivity.—As noted on page 78, the conductivity of solutions is affected greatly by the temperature. In conductors of the first class, such as metals, the conductivity is *decreased* by an elevation in temperature; while in conductors of the second class, such as solutions, the conductivity

is *increased* by raising the temperature, owing principally to increased mobility of the ions. This change amounts to about 2 per cent for each degree Centigrade (or 1.1 per cent for each degree Fahrenheit). It is therefore apparent that even a slight change in temperature of the solutions, such as may occur during operation, *e.g.*, from 20 to 40°C. (68 to 104°F.), may produce an increase of 40 per cent in the conductance (or a decrease of 30 per cent in the resistance) of a bath; and at still higher temperatures, *e.g.*, in solutions heated intentionally to 70°C. (158°F.), the conductance may be nearly doubled (*i.e.*, the resistance reduced to one-half). Where, then, the use of warm solutions produces deposits having desired properties, heating of the solutions may prove very economical in the consumption of electrical energy.

7. HEAT PRODUCED BY ELECTROLYSIS

It is frequently desirable to employ cool solutions in order to obtain deposits having certain desirable properties. In such cases the heat developed in a solution by the passage of a current must be taken into consideration. On page 56 it was shown that the energy consumed in the passage of a current, *e.g.*, through a solution, is equal to the power multiplied by the time; and that Energy (in joules) = Electromotive force × Current × Time = EIt
But since $E = IR$, we may also write: Energy = $IR \times It = I^2Rt$.

In the simple ideal electrolysis, in which there is no evolution of hydrogen or oxygen, and in which the anode and cathode are alike both physically and chemically, all the energy expended in the passage of the current is converted into heat. The amount of heat produced may be expressed in joules, but it is more convenient to employ the "calorie," which is the quantity of heat required to raise the temperature of 1 g. of water 1°C. A joule is equal to 0.239 cal.

The above equation may therefore be written:

$$\text{Calories produced by electrolysis} = I^2Rt \times 0.239$$

or if we consider a period of 1 second (in which case $t = 1$), we may state that the rate of heating is proportional to the resistance and to the square of the current. This relation is important, since it determines the relative heating effect produced by any change in operating conditions. The application of this formula may be readily illustrated.

Problem.—A certain bath, A, has a resistance of 0.1 ohm, so that when an e.m.f. of 5 volts is applied, a current of $\frac{5}{0.1} = 50$ amp. is produced. Suppose now, that by appropriate additions to the solution the resistance of the bath (now called B) is decreased to 0.05 ohm (*i.e.*, the conductance is doubled). What will be the relative heating effect in A and B, (*a*) when the e.m.f. is maintained at 5 volts, and (*b*) when the current is maintained at 50 amp.?

The heat produced (in joules) per second is equal to I^2R, therefore

In A, Heat $= 50^2 \times 0.1 = 50 \times 50 \times 0.1 = 250$ joules per second.

In B, (*a*) with 5 volts:

$$I = \frac{E}{R} = \frac{5}{0.05} = 100 \text{ amp.}$$

Therefore Heat $= 100^2 \times 0.05 = 100 \times 100 \times 0.05 = 500$ joules per second.

(*b*) with 50 amp. (which will require only 2.5 volts)

$$\text{Heat} = 50^2 \times 0.05 = 50 \times 50 \times 0.05 = 125 \text{ joules per second}$$

(The same relative results would be obtained if all these values were changed to calories by multiplying each by 0.239.) These calculations show that if the resistance of a bath is decreased and the voltage is kept constant, the heat produced will be *greater* because of the higher current which flows. If, however, the voltage is adjusted so as to maintain a constant current, the heat produced in the bath is *decreased* when the resistance of the bath is decreased. An understanding of this relation removes the apparent inconsistency which many platers and electrotypers have noticed, that when sulphuric acid is added to an acid copper solution, and the *same voltage is applied*, the solution is heated *more*, in spite of the fact that the conductivity has been increased. If the voltage has been reduced to yield the same current (or current density), *less* heat would have been produced.

The *temperature* reached by the bath as a result of electrolysis depends upon the rate at which heat is produced, the volume of the bath, and the rate at which the heat is being carried away. This latter rate depends upon the temperature of the room; upon the heat conductivity of the tank walls (*e.g.*, a stoneware tank conducts heat much more rapidly than a wooden tank); upon the rate of evaporation of the solution (which in turn depends upon the temperature and humidity of the air); and upon the amount of heat conducted away by the hangers and busbars, and by the air if air is used for agitation. Most of these factors are difficult to measure and control, and hence

any calculation of the temperature likely to be reached in any bath is at best only a very rough approximation. The question is often asked: "What volume of solution should be used to plate a certain *area* of work?" Assuming that the temperature reached in the bath is the governing factor, it is possible, but not practicable, to calculate the relation between volume of solution and the area of work (or, better, the total current to be used) for a solution of a certain resistivity, or requiring a certain voltage. From purely empirical observations it may be stated that under the usual average conditions it is possible to dissipate continuously energy equal to about 1 watt (*i.e.*, 1 joule per second) per liter of solution, or about 4 watts per gallon, without the temperature rising more than about 10°C. (18°F.) above the room temperature. Thus in an acid copper bath containing about 1,000 l. (270 gal.), and operated with a 1-volt drop between anodes and cathodes, 1,000 amp. may be passed without the temperature rising more than the above amount. In a corresponding nickel bath requiring, for example, 4 volts for operation, a current of 250 amp. will produce about the same heating effect. These figures are at best, however, only a rough approximation.

CHAPTER VII

FACTORS GOVERNING THE CHARACTER AND DISTRIBUTION OF THE DEPOSITS

The principles discussed in the two preceding chapters relate chiefly to those factors which determine the efficiency of the electrodeposition processes and therefore the relative cost of the current used in depositing a certain quantity of metal. Such considerations are important, especially in large plants, or where relatively cheap articles are plated. Nevertheless, it must be admitted that the percentage cost for electricity and material in the production either of electrotypes or of electroplated articles is usually so small that very properly far less attention is given to it than to the quality of the work produced or the labor required to yield a satisfactory product. The smoothness, the brightness, the hardness (or softness) which may be desired in any given product are determined in large measure by the physical structure of the deposited metals. A knowledge of the conditions which influence this structure is therefore important, since such knowledge, even when imperfect, often permits the prediction of those conditions or changes which will yield a product having certain desirable properties. Without a knowledge of such factors, the practical plater or electrotyper is usually forced to try numerous and sometimes expensive measures to avoid some defect in operating conditions. It must be stated frankly, however, that there are still many unknown factors which influence the character of the deposits, and hence the following discussion should not be considered as in any sense complete.

Examination with x-rays has shown that all electrodeposited metals have a crystalline structure, and that the principal differences in the appearance and physical properties of the deposited metal are caused by differences in the size or shape of the individual crystals. In those cases in which the metal appears with the naked eye, or even under considerable magnification, to be amorphous or non-crystalline, examination of the surface with

higher magnification or a study of a cross-section after etching invariably shows that the metal has some characteristic structure. Where through the use of addition agents very bright deposits are secured, or particles with rounded surfaces are produced, it is probable that the crystal structure is simply modified, and not eliminated. Such expressions as "non-crystalline" or "amorphous" deposits really mean "very fine-grained" deposits.

In general, it may be stated that within certain limits the finer the crystals of a deposited metal, the brighter, smoother, stronger, and harder will be the deposit. Where, therefore, bright or dense deposits are desired, the effort should be made to select those conditions which will produce very fine crystals; while if "matte" deposits are desired, conditions for producing relatively coarse crystals should be sought.

If, then, the process of electrodepositing metals depends upon the formation of crystals, however small, it seems reasonable that the principles of ordinary crystal growth must apply in some degree to the formation of crystals by electrodeposition. A consideration of these principles in 1904 led W. D. Bancroft[1] to state certain "axioms," *i.e.*, self-evident truths, regarding the structure of electrodeposited metals.

These "axioms" were stated by Dr. Bancroft in the following terms:

1. Bad deposits are due to excessive admixture of some compound or to excessively large crystals.
2. Excessive admixture of any compound can be eliminated by changing the conditions so that the compound cannot precipitate.
3. Increasing the current density, increasing the potential difference at the cathode, or lowering the temperature decreases the size of the crystals.
4. The crystal size is decreased when there are present, at the cathode surface, substances which are adsorbed by the deposited metal.
5. If a given solution will give a good deposit at any current density, it will give a good deposit at any higher current density, provided the conditions at the cathode surface are kept constant.
6. Treeing is facilitated by a high potential drop through the solution and by conditions favorable to the formation of large crystals.

Partly because of the scientific terms used in these statements, but mostly because of a lack of definite and reliable data, these axioms have received all too little consideration or application

[1] *Trans. Am. Electrochem. Soc.*, vol. 6, p. 27, 1904, and vol. 23, p. 266, 1913.

either by electrochemists or electroplaters. In order to illustrate and emphasize them, a number of simple experiments were carried out several years ago at the Bureau of Standards.[1] While these few experiments do not, of course, prove that these axioms apply to all cases in electrodeposition, much less that they are the only important factors, the results furnish good evidence of their value in research and practice, at least as a basis from which to proceed further. These experiments will be referred to in the following pages, using the copper deposits as illustrations. For details the original paper should be consulted.

Experiments were made with corresponding solutions of copper, zinc, and nickel, of which in all cases simple "standard" solutions were operated for purposes of comparison. These "standard" solutions, which were selected from the standpoint of simplicity, and not as commercially practicable solutions, had the following composition:

1. Copper sulphate N (125 g./l., or 17 oz./gal.)
   Sulphuric acid 0.1 N (4.9 g./l., or 0.7 oz./gal.)
2. Zinc sulphate N (144 g./l., or 19 oz./gal.)
   Boric acid 0.1 N (6.2 g./l., or 0.8 oz./gal.)
3. Nickel sulphate 0.8 N (112 g./l., or 15 oz./gal.)
   Nickel chloride 0.2 N (24 g./l., or 3.2 oz./gal.)
   Boric acid[2] 0.1 N (6.2 g./l., or 0.8 oz./gal.)

In all cases the deposits were produced upon the same metals, *i.e.*, copper on copper, etc., in order to avoid deposition by immersion. Unless otherwise stated, deposits to be compared with each other were always of about the same thickness, usually 0.025 mm. (0.001 in.), which is above the average thickness of most electroplated deposits.

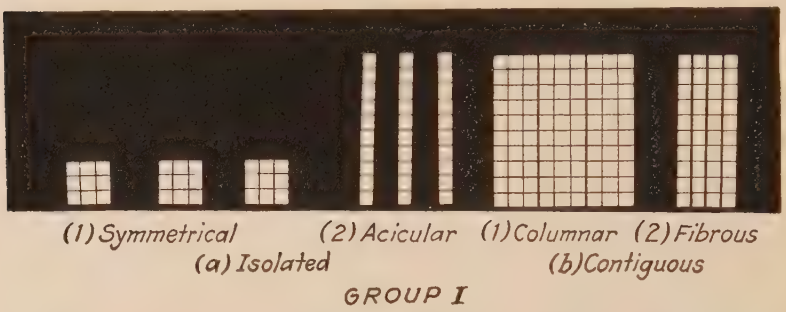
More recently a paper has been published[3] in which the types of crystals observed in electrodeposited metals are classified, and certain principles are discussed. These principles are in general consistent with those involved in Bancroft's axioms, and will be referred to in the following discussion. It should be clearly recognized however, as has been pointed out in several recent

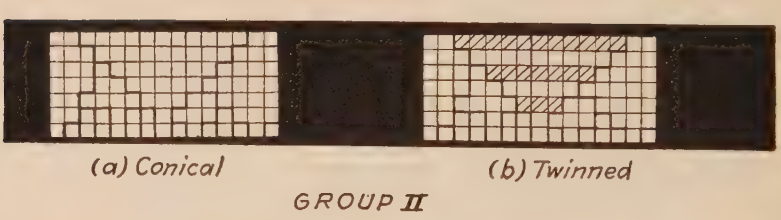
[1] *Trans. Am. Electrochem. Soc.*, vol. 36, p. 213, 1919.

[2] When the normality of boric acid, H_3BO_3, is referred to, it is assumed to be monobasic. A normal solution therefore contains 62 g./l. of H_3BO_3.

[3] Blum, W., and Rawdon, H. S., *Trans. Am. Electrochem. Soc.*, vol. 44, p. 397, 1923.

papers by Kohlschüetter, Foerster, Graham and others, that at best these principles are only a rough guide, and that there are numerous observations that cannot be, or at least have not been, reconciled with them. In many cases however they are of value





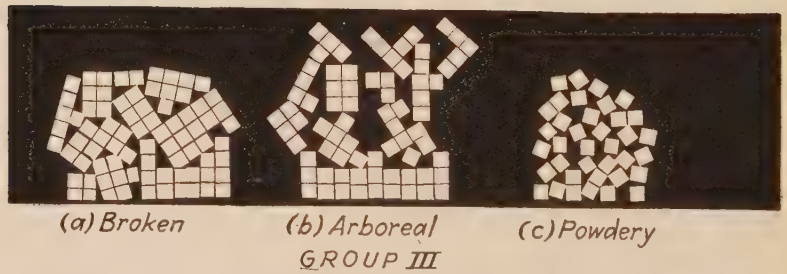


FIG. 8.—Diagrammatic Representation of Principal Crystal Types.

in permitting useful predictions of how to change the properties of a deposit in any desired direction.

In Fig. 8 are illustrated diagrammatically the various types of crystals, actual pictures of which are given in the following pages. The principal conclusion of the above paper was that any factor which increases the cathode polarization tends to

change the crystal structure from Group I to II to III, and vice-versa. The effects of various factors such as solution composition, current density, temperature and agitation will be separately considered from this standpoint.

1. CURRENT DENSITY

The effect of the current density or rate of deposition is of special interest to electroplaters and electrotypers, as it is usually desirable to produce a certain result in the shortest possible time, and thereby maintain a maximum output. It is therefore very important to determine the effect which is produced upon the quality by an increase in current density. Bancroft's statement

a b c

FIG. 9.
20 diam.
Copper Deposits.
a 0.2 amp./sq. dm. (1.9 amp./sq. ft.)
b 2 " " " (19 " " " ")
c 3 " " " (28 " " " ")

that "increasing the current density decreases the size of the crystals" at first appears to be contrary to practical experience, which has shown that a rough or "burnt" deposit is caused by too high a current density for the other conditions such as concentration, acidity and temperature. Up to a certain current density, however, it was found in these experiments that finer grained deposits are produced by increasing the current density. This is illustrated for copper in Fig. 9, where the *b* deposit is finer grained than that marked *a*. The actual difference in the size and type of the individual crystals produced at low and high-current densities is shown in Fig. 10, which represents a cross-section of thick copper deposits. The deposit in Fig. 10*a*

has a typical "conical structure," while that in 10*b* is "broken" (Group IIIa), *i.e.*, it has a random structure.

When the current density is still further increased there is a tendency, most marked in acid copper solutions, to produce "treed" ("arboreal") deposits, (Group IIIb) especially on edges and corners where the current density is usually much higher than the average. Such trees as illustrated in Fig. 11, consist of very small crystals, although they may appear like large crystals.

Finally when the current density is quite excessive, powdery or "burnt" deposits (Group IIIc) are produced. These usually contain some basic material such as the hydroxide or a basic

a b

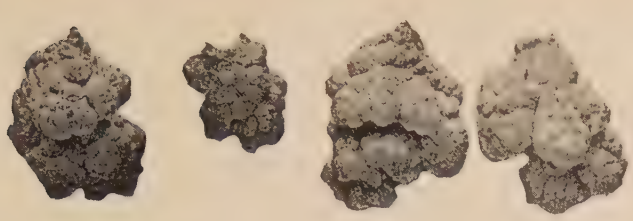
FIG. 10
300 diam.
Copper Deposits.
Effect of Current Density.
a 4 amp. /sq. dm. (37 amp./sq. ft.)
b 10 " " " (93 " " ")

salt of the metal. Such compounds precipitate because as the current density is increased, the pH of the cathode film also usually increases.

All these changes are consistent with the fact that as the current density is increased, the cathode film becomes impoverished in metal and metal ions, and hence the polarization increases.

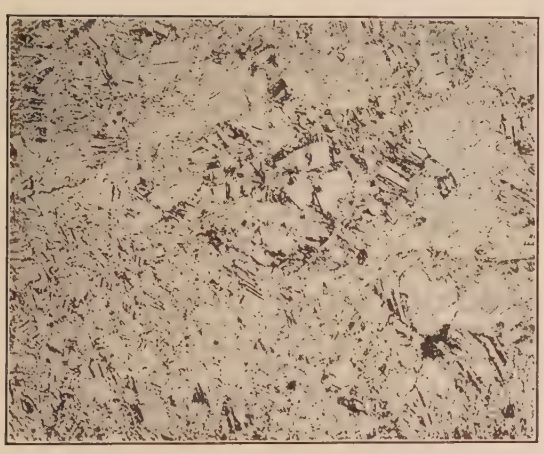
2. CONCENTRATION AND AGITATION

If the cause of "burnt" deposits at any given current density is the local impoverishment of the metal content of the solution, then it should be possible to produce good deposits at a higher



a Natural size

b × 2.5



c × 100

FIG. 11.—Structure of Arboreal or Treed Deposits.
a. Copper trees.
b. Cross section.
c. Cross section.

current density, by providing an increased metal supply. This can be accomplished either by actually increasing the metal concentration of the solution, or by bringing to the cathode a fresh supply by means of suitable agitation. Both of these methods decrease the cathode polarization. The use of very concentrated solutions is often inconvenient and expensive and generally reduces the anode efficiency, but by suitable agitation the use of more dilute solutions may be permitted. That the effect of agitation is more pronounced *at a given current density* in

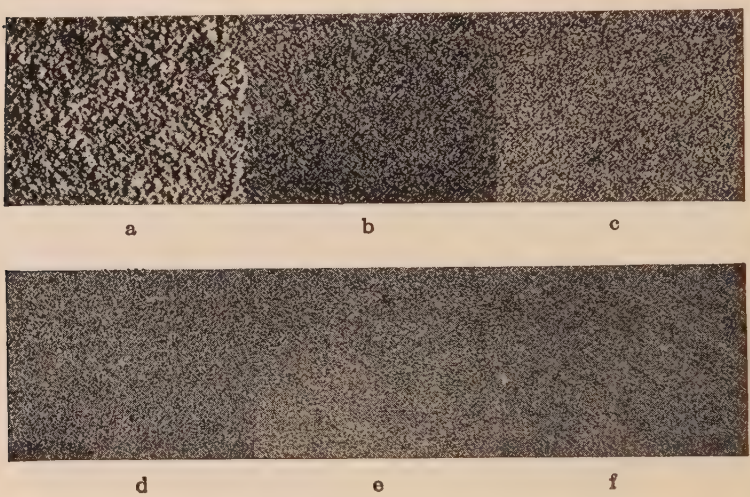


FIG. 12.
20 diam.
Copper Deposits.
Effect of Agitation.

a Still solutions 0.5 *N*
b Air agitation 0.5 *N*
c Mechanical agitation 0.5 *N*
d Still solution 2 *N*
e Air agitation 2 *N*
f Mechanical agitation 2 *N*

dilute than in concentrated solutions is shown in Fig. 12 where the deposits shown are from solutions which are respectively one-half and twice the concentration of the "standard" solutions. Another beneficial effect of agitation is expecially marked in zinc deposition, *i.e.*, the sweeping away of bubbles of gas from the cathodes.

If agitation is advantageous, it at first appears strange that so much electroplating is conducted in still baths. One practical objection to agitation in electroplating is that sediment is thereby kept in suspension, and by lodging upon the cathodes causes

roughness of the deposits. In barrel plating this tendency to roughness is at least partly counteracted by the burnishing action which occurs. In electrotyping, air agitation is used almost universally in both the acid copper and the nickel solutions. This is permissible because, in electrotyping, a slight roughness on the *back* of the deposits is not objectionable. Other objections to agitation, especially by air, are (1) that it usually decreases throwing power, (2) in cyanide solutions agitation favors the formation of carbonates, and (3) in brass plating the color is greatly influenced by agitation. In spite of these objections, there has been a tendency in recent years to introduce moderate agitation, *e.g.* (1) in mechanical conveyor systems, (2) by moving cathode rods, and (3) in tanks in which the solution is continuously circulated and filtered. In all of these methods it is possible to use higher current densities than can be used in still baths.

3. TEMPERATURE

It is important to know the effect of the temperature of the solution upon the character of the deposits, not only because a

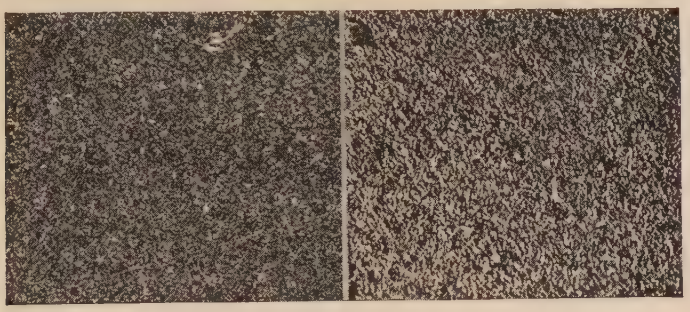


FIG. 13.
Copper Deposits.
Effect of Temperature.
a 25°C. (77°F.)
b 65°C. (149°F.)

means is thereby furnished for intentionally producing deposits of any desired structure, but also because even those accidental temperature changes which occur during operation or at different seasons may cause great variations in the quality of work produced. Bancroft's statement that "lowering the temperature decreases the size of the crystals" was fully confirmed in experi-

ments in which the temperature varied from 25°C. (77°F.) to 65°C. (149°F.). In every case the crystal structure of the deposits produced at higher temperatures was coarser than those produced at low temperatures, as illustrated in Fig. 13. (With nickel the effect is similar, but much less marked.) The actual difference in the size of individual crystals of copper deposits is shown in Fig. 14. In general an increase in temperature decreases the cathode polarization and produces such changes in structure as are shown. In this figure deposit (a) is a good illustration of twinned crystals (Group IIb), while deposit (b) represents a conical structure (Group IIa). This change is in the direction predicted on p. 88.

a FIG. 14. b
300 diam.
Copper Deposits.
Effect of Temperature.
a 25°C. (77°F.)
b 40°C. (104°F.)

That such differences as are produced by moderate temperature changes are significant is indicated by the fact that copper electrotyping deposits similar to those pictured in Fig. 14a have an ultimate tensile strength of about 2,800 kg./cm.^{2} (40,000 lb./sq. in.) and deposits similar to those shown in Fig. 14b have a strength of only 1,400 kg./cm.^{2} (20,000 lb./sq. in.), and are much softer and more easily abraded. It was found in a study of electrotyping that the temperature had a more marked effect upon the properties of electrodeposited copper than did any other single factor.

In spite of the fact that, at a given current density, increasing the temperature of solutions produces coarser crystals, warm

solutions are frequently employed successfully in commercial work. Where heated solutions are used the benefits are due to other causes, such as (*a*) an increase in the solubility of the salts, which may permit the use of higher concentrations and consequently higher current densities; (*b*) an increase in conductivity, which reduces the tendency to treeing and also produces higher current densities (at a given voltage), and thereby reduces the crystal size; (*c*) a change in the pH of the solution; or (*d*) a decrease in the occlusion of hydrogen, which occlusion in the case of nickel, chromium and iron is one of the causes of cracked deposits. These considerations indicate that in the choice and definition of operating conditions, a number of factors, some of which may tend to counteract each other, must be considered. The actual product obtained is the net result of all of these factors. Nevertheless it is important to distinguish the effects of the individual factors wherever possible.

4. CONDUCTIVITY

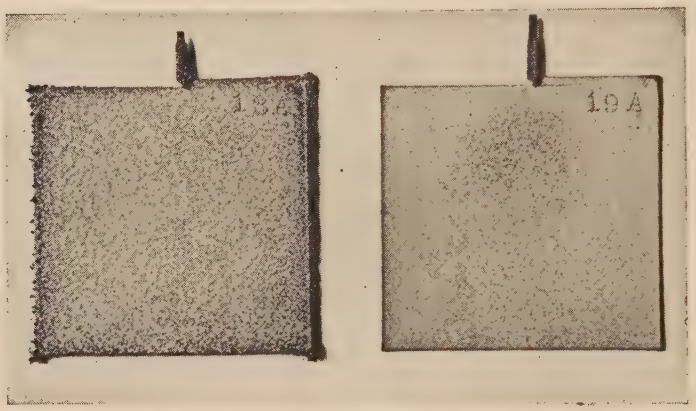
The use of well-conducting solutions is an obvious economic advantage, as it reduces the voltage required to produce any given current density and thereby reduces the power costs. Good conductivity is also important because it reduces the tendency toward the formation of trees or rough deposits. This latter statement is simply another form of Bancroft's axiom that "treeing is facilitated by a high potential drop through the solution," as *at a given current density* the conductivity of the solution governs the potential drop through it. Thus it was found that in the acid copper bath, such as is used in electrotyping, an increase in the content of free sulphuric acid from 0.1 *N* to 1.1 *N* (*i.e.*, from 5 g./l., or 0.67 oz./gal., to 54 g./l., or 7.2 oz./gal.) decreased the specific resistivity at 25°C. (77°F.) from 22.4 to 4.9 ohm-cm., and greatly reduced the tendency to form trees (Fig. 15). In nickel and zinc solutions it was found that if the conductivity was increased by the addition of sodium chloride, there was far less tendency to form trees. The use of well-conducting solutions is therefore especially desirable where thick deposits are to be made, as in electroforming.

On the other hand it should be emphasized that while good conductivity is advantageous for the above reasons, it is by no means the most important factor in electrodeposition. In some cases an increase in conductivity actually decreases the cathode

efficiency. It is necessary in such cases to determine whether the advantages of good conductivity outweigh its disadvantages.

5. METAL ION CONCENTRATION

According to the theory of electrolytic dissociation, all salts in aqueous solution are dissociated, in some degree at least, into positively charged metal ions, or cations, and negatively charged non-metallic ions, or anions. It is only through the direct or indirect discharge of metallic ions that it is possible to deposit any metal electrolytically. It would therefore appear that the favorable condition for producing metallic deposits would be



a FIG. 15. b
¾ size.
Copper Deposits.
Effect of Conductivity Upon Treeing.
a Copper sulphate *N*, Sulphuric acid 0.1 *N*.
b Copper sulphate *N*, Sulphuric acid 1.1 *N*.

the presence of a large number of metallic ions. Under such conditions each crystal of metal would be surrounded by a large number of metal ions, so that by the passage of the current it could grow rapidly. This is exactly what happens in a solution rich in metal ions. But if fine-grained deposits are desired, it is essential to select conditions which will be unfavorable to the growth of a few crystals, and will thereby foster the production of a large number of (necessarily) smaller crystals. This condition is fulfilled when there are not *at any given time* many metal ions in the solution—in other words, an individual crystal does not have many ions adjacent to it to permit its growth.

One method for reducing the metal ion concentration is to use a very dilute solution. But if this course is adopted, the passage of a current soon removes the metal ions which are present and there is insufficient metal available to be discharged, and burnt or spongy deposits result. If, however, a solution can be secured which contains only a few metal ions, but a large amount of dissolved metal salt which will furnish a fresh supply of ions nearly as fast as they are removed, the solution will be favorable for the production of fine-grained deposits. This condition is fulfilled in solutions containing a "complex salt" of a metal, such as is present in a metal cyanide solution. Thus in a cyanide zinc solution, we may assume that the principal compound present is sodium zinc cyanide, $Zn(CN)_2.2NaCN$, or $Na_2Zn(CN)_4$. This compound when dissolved dissociates largely in the following way:

$$Na_2Zn(CN)_4 \leftrightarrows 2Na^+ + Zn(CN)_4^{--}$$

forming not zinc ions, but sodium ions and a complex anion containing the zinc. This latter ion in turn dissociates to only a very slight extent to form zinc ions, thus

$$Zn(CN)_4^{--} \leftrightarrows Zn^{++} + 4CN^-$$

If, however, these few zinc ions are discharged to deposit zinc, a few more ions are at once liberated. The actual metal ion concentration of zinc and copper in their cyanide solutions is very small, and therefore these solutions exhibit in a marked degree the property of producing fine-grained deposits (Fig. 16).

According to another theory, the reason that fine-grained deposits are produced from solutions containing complex ions is that in such solutions the current first discharges at the cathode the more negative metal (sodium in the case of sodium zinc cyanide) and that this metal in turn precipitates the zinc (or other metal present in the complex ion). There is no conclusive evidence to show that the metal is deposited by secondary reaction; and such an explanation complicates instead of simplifying the process.

It is possible to reduce slightly the metal ion concentration of any salt solution by the addition of a substance with a "common ion." Thus if sodium sulphate is added to a copper sulphate solution, the number of copper ions is materially decreased. A similar effect is produced by adding sodium sulphate (or any

other soluble sulphate) to zinc or nickel sulphate solutions. In normal salt solutions, it is possible to reduce the metal ion content to less than 10 per cent of its usual value by the addition of a common ion. Since the reduction in metal ion concentration thus produced is less marked than in the cyanide solutions, there is less effect upon the crystal size, although the effect of such additions is usually perceptible.

The beneficial effect of a low metal ion concentration is indicated in Bancroft's statement that "increasing the potential difference at the cathode decreases the size of the crystals." This is consistent with the statement that increasing the cathode

a b c

FIG. 16.
20 diam.
Copper Deposits.
Effect of Metal Ion Concentration.
a "Standard" solution.
b " " + *N* Sodium sulphate.
c Cyanide solution.

polarization usually decreases the crystal size. In general the polarization increases more rapidly in solutions with a low metal ion concentration, such as the complex cyanides, than in simple salt solutions.

6. HYDROGEN ION CONCENTRATION

From Table 10 (appendix), we would at first assume that the metals, such as zinc, lead, iron, etc., which are above hydrogen in this series, could not be deposited from acid solutions, because in such solutions, which contain a considerable number of hydrogen ions, the latter would be discharged more readily than the metal. Actually, however, it is possible to deposit zinc from a solution containing appreciable free acid, since, as explained

on page 74, the overvoltage of hydrogen on zinc is sufficient to permit the separation of the zinc before the hydrogen. Even in such solutions it is necessary to limit the acidity in order to secure a high cathode efficiency and a dense deposit. In the case of iron and nickel, however, the hydrogen overvoltage is low and therefore it is necessary to employ more nearly neutral solutions. Copper, which lies below hydrogen in the series, can be deposited from solutions containing concentrations of free acid greater than that of the metal. Similarly, gold and silver can be deposited from strongly acid solutions, but not in a form which is of interest to electroplaters.

A clear distinction should be made between the concentration of *acid* present in the solution, as determined, *e.g.*, by a direct titration, and the *acidity* of the solution, or its *hydrogen ion* concentration. The first is a measure of the *quantity*, and the latter of the *intensity* of the acid present. It appears probable that in most cases in metal deposition the hydrogen ion concentration is more important than the content of acid.

The first and most important effect of hydrogen ion concentration is its relation to the structure of the deposit as a whole, since with such metals as zinc the presence of excessive acidity, and consequent low efficiency, fosters the production of spongy and porous deposits; and with iron and nickel, of pitted, cracked, and curled deposits. This latter behavior is probably due to the solubility of hydrogen in iron and nickel, with the formation of brittle "alloys." The determination and regulation of the hydrogen ion concentration of solutions of zinc, nickel, and iron should therefore result in the production of more uniformly satisfactory deposits. Many empirical methods have been employed to regulate the acidity of plating solutions, principally by the use of weak acids, such as boric, acetic, tartaric, or citric acids (or their salts); but very few actual measurements of hydrogen ion concentration were made until within the last 5 years.

Various methods have been proposed for expressing the hydrogen ion concentration, all of which are based upon the relative normality. A solution normal in hydrogen ions will contain in each liter 1 g. equivalent, or, for practical purposes, 1 g., of hydrogen ions. In dealing with relatively strong acid solutions it is convenient to express the hydrogen ion concentration in terms of the fractional normality, thus $[H^+]$ (hydrogen

ion concentration) = 0.1 N, etc. If, however, we are dealing with weakly acid solutions, as is the case in nickel deposition, it would be inconvenient to refer to $[H^+] = 0.00001$ N. These expressions can be shortened by the use of powers of ten, *i.e.*, of exponents, in which case the latter value becomes $[H^+] = 10^{-5}$ N; which is read "ten to the minus fifth normal." In order still further to simplify the expression of these low acidities, Sörensen proposed to employ simply the numerical exponent, the cologarithm of $[H^+]$, which he designated, as the "pH" of the solution. Thus in the above solution, pH = 5. The relation between these different methods of expressing hydrogen ion concentration is shown in the following table.

METHODS OF EXPRESSING HYDROGEN ION CONCENTRATION IN TERMS OF NORMALITY

Fraction	Decimal	Exponential	pH
1/10	0.1	10^{-1}	1
1/100	0.01	10^{-2}	2
1/1,000	0.001	10^{-3}	3
1/10,000	0.000,1	10^{-4}	4
1/100,000	0.000,01	10^{-5}	5
1/1,000,000	0.000,001	10^{-6}	6
1/10,000,000	0.000,000,1	10^{-7}	7
1/100,000,000	0.000,000,01	10^{-8}	8
.....	.....	....	..
etc. to			
1/100,000,000,000,000	0.000,000,000,000,01	10^{-14}	14

Throughout this book the pH system of expression will be employed. In this system, an *increase* in pH represents a *decrease* in hydrogen ion concentration, *i.e.*, the solution is less acid, or more alkaline. In the above table a pH of 7 represents the neutral point, *i.e.* the reaction of perfectly pure water (p. 31). Any solution with a pH greater than 7 is alkaline with respect to pure water. The pH scale is therefore a scale of alkalinity as well as of acidity. All cyanide plating solutions are alkaline, and probably correspond to pH 9 to 12. Very few measurements of the pH of cyanide plating solutions have been made or published.

The various methods for measuring hydrogen ion concentration are described in a book by W. M. Clark.[1] Direct measure-

[1] "The Determination of Hydrogen Ions," 3rd ed., Williams & Wilkins Co., Baltimore, Md., 1928.

ment by means of a hydrogen electrode furnishes the basis of all pH values. This method requires rather elaborate apparatus, and, moreover, is not applicable to such solutions as contain oxidizing substances or certain metallic salts.

In recent years the "quinhydrone electrode" has been proposed and used for measuring the pH of nickel plating solutions. The equipment employed is similar to that used with a hydrogen electrode, but the measurements can be made more quickly. The principle of the method is that the potential of a metal such as gold, when immersed in a solution containing quinhydrone (and hydroquinone, which is automatically formed from it) depends upon the hydrogen ion concentration. The relation of the results with quinhydrone and with indicators will be discussed under nickel (p. 270). For control of plating solutions, colorimetric measurements with appropriate indicators have been most extensively used. Recently (see p. 270) it has been found that due to "salt errors" the colorimetric values in most nickel solutions are about 0.5 pH higher than the values with the hydrogen or quinhydrone electrode. Suitable corrections should therefore be made to put all results on a comparable basis.

The principle of colorimetric methods is that of comparing with a suitable standard the color produced by adding a definite quantity of the proper indicator to a sample of the solution. In effect, this method is simply an extension of the familiar method of determining whether a substance is acid or alkaline by noting the color which it produces with an indicator such as litmus, except that, to make definite measurements of hydrogen ion concentration, it is necessary to employ a number of indicators which are sensitive in different ranges of pH or hydrogen ion concentration. For details of making such measurements suitable texts, such as that of Clark, should be consulted. The application of such measurements to the regulation of nickel solutions is described on page 267. In general, it may be stated, as a result of such measurements, that the ideal plating solution for such metals as require a nearly neutral solution is one which is well "buffered," *i.e.*, its pH should not change rapidly within the desired working range upon the addition of small amounts of acid or of base, such as are in effect introduced by variations in anode and cathode efficiency.

The cause of the effect of the hydrogen ion concentration upon the microstructure of the deposits has never been quantitatively

determined. Qualitative observations show that deposits of zinc, nickel, and iron are brighter and therefore finer grained in solutions possessing a relatively high acidity (or low pH). Thus in nickel plating, the production of a very bright deposit (in solutions free from addition agents) is an evidence of acidity in the solution, and frequently serves as a danger mark or warning that the solution is close to the point at which cracked or curled deposits will be produced. No definite cause has been shown for the formation of brighter deposits in acid solutions than in more nearly neutral solutions. It may be associated with the actual solution of hydrogen in the metal, or may be due to the absence of basic material such as may be present in minute amounts in the ordinary less bright deposits.

7. ADDITION AGENTS

In the literature[1] upon electrodeposition, frequent reference is made to "addition agents," *i.e.*, substances which when added to solutions bring about the production of very smooth or bright deposits, or permit the use of higher current densities. It is very difficult to define the term "addition agent," since in the broadest sense it includes all substances, other than the metallic salt and water, which are added to the solution for any purpose whatever. As above explained, certain substances are added to solutions for the purpose of increasing the conductivity, or decreasing the metal ion concentration of solutions, or for regulating the acidity or hydrogen ion concentration. Since these functions are fairly definite and well understood, it is most convenient to designate as "addition agents" those substances which do not produce any marked effect upon the conductivity, metal ion concentration, or hydrogen ion concentration of solutions, but which do influence the structure of the deposits. Such a negative definition is arbitrary, but it may serve until a more accurate conception is gained of the functions and classification of addition agents.

As thus defined, addition agents may conveniently be divided into two classes, *viz.*, colloidal and crystalloidal substances.

[1] Reviews of this subject may be found in "The Rôle of Colloids in Electrolytic Metal Deposition" by Henry J. S. Sand, on p. 246 of the *4th Report on Colloid Chemistry*, of the Dept. of Sci. and Ind. Res., Brit. A. A. S., 1922; and "Colloids in the Electrodeposition of Metals" by W. Blum, on p. 301 of the Colloid Symposium monograph, 1928.

There is, however, no sharp distinction between these two groups, since many crystalloidal substances may cause the formation of colloidal products.

The term "colloid" was originally applied to those substances, such as glue, gelatin, albumen, etc., which are amorphous or non-crystalline and which have the property of forming jelly-like products under certain conditions. As a result of investigations in recent years, the term has, however, acquired a much broader meaning, and "colloid chemistry" is a distinct and important branch of science. The modern conception of colloids can best be explained through a consideration of colloidal solutions. When a crystalline substance, such as ordinary salt, is dissolved in water, it is believed that the solution contains sodium chloride molecules and sodium ions and chloride ions. All of these particles are of such small dimensions that it is not possible to see or detect them even by the use of the highest magnifications or by the ultramicroscope. Such a solution is said to be "optically clear." If, however, a small amount of gelatin is dissolved in water, and the apparently transparent solution obtained is examined by an ultramicroscope (which projects a very powerful light beam through it), it is possible to detect, in suspension in the water, particles which are in constant motion. These colloidal particles, although very small, are larger than the molecules or ions which exist in true solutions.

These colloidal particles have the power to take up or "adsorb" ions from solutions, thereby either becoming electrically charged or neutralizing electrical charges already existing upon them. In the latter case they are coagulated, or precipitated. A familiar example of such coagulation is the action of a weak acid, such as acetic acid, upon a solution containing the white of egg or albumen, which is thereby coagulated. When a solution containing dissolved colloids is subjected to electrolysis, positively charged colloids migrate to the cathode, and negatively charged to the anode. The direction of such migration is sometimes determined by the acidity or alkalinity of the solution.

The indications are that in order for a colloid to have any effect upon the structure of a deposited metal, it must, upon electrolysis, migrate to the cathode, where it may be taken up or adsorbed by the deposited metal. It has been shown by numerous investigators that in many deposits obtained from solutions

containing even small amounts of colloids, there are appreciable amounts of organic matter of at least similar composition. Thus a deposit of copper from an acid copper solution containing glue has been found to contain organic matter, which upon heating has the characteristic odor of decomposed nitrogenous compounds.

Proteins such as gelatin have an "iso-electric point," at a pH of about 4.7, at which they are electrically neutral and do not migrate to either the anode or cathode. Frölich[1] has shown that at a pH of less than 4.7, *e.g.* in an acid copper solution, such colloids are positively charged and migrate not only toward but to the cathode surface, and are actually included in the cathode deposit. In a zinc solution, even with a pH less than 4.7, gelatin is not included in the deposit, although it does migrate toward the cathode and influences the cathode polarization and the structure. This is because the cathode film in zinc deposition usually has a pH higher than 4.7, hence in this cathode film the gelatin no longer migrates to the cathode.

The effect of colloidal particles is included in Bancroft's fourth axiom that "the crystal size is decreased when there are present, at the cathode surface, substances which are adsorbed by the deposited metal." There is, however, very little understood about the mechanism of such effects of colloids, much less about the behavior of specific colloids in any given solution. One theory assumes that all metals at the moment of liberation are amorphous, but immediately thereafter assume a crystalline state, unless there are present in the solution "protective colloids" or other substances which favor the preservation of the colloidal state. Another explanation of the effect of colloids is that of the "movable diaphragm."[2] According to this theory the colloids are carried by the current to the cathode, and there discharged. Since upon any point or projection on the cathode the current density is higher than the average upon the entire surface, it follows that a larger amount of colloid must be deposited upon the points than elsewhere, and hence the polarization and resistance are increased at those points. In consequence, the current density decreases there and increases at other parts of the surface, until the same process is repeated there. The net result is that smaller crystals are produced and the formation of trees is

[1] *Trans. Am. Electrochem. Soc.*, vol. 46, p. 67, 1924.

[2] Englehardt, V., *Trans. Am. Electrochem. Soc.*, vol. 21, p. 332, 1912.

prevented. It has been recently shown by Fuseya[1] that substances such as citric acid and tartaric acid, which produce finer grained deposits of copper and silver, form complex ions in the copper or silver solutions. It is at least possible that colloids may also form complex ions with the metals and be discharged upon the cathode.

FIG. 17.
Structure of Heavy Copper Deposits (× 100).

Current Density	Ultimate Tensile Strength
6.5 amp./dm.^{2}	1700 kg./cm.2
60 amp./sq. ft.	24,000 lb./sq. in.

It is entirely reasonable to assume that the effect of any foreign substance which is actually adsorbed by or included in the deposit will be to hinder the normal growth of individual crystals, and thereby assist the formation of fine-grained deposits. This may be illustrated by the effect of actual layers of one metal interposed between layers of another. If thick deposits of copper are produced from an acid copper

[1] *Trans. Am. Electrochem. Soc.*, vol. 50, p. 235, 1926; and vol. 52, p. 249, 1927.

solution, the individual crystals grow to a considerable size (Fig. 17) and there is a marked tendency to treeing. If, however, even thin layers of nickel are deposited upon the copper at intervals, the copper subsequently deposited is much finer grained (Fig. 18), and there is much less treeing. Deposits thus produced, and consisting of alternate layers of copper

FIG. 18.

Structure of Alternate Deposits of Copper and Nickel (× 100)

Thickness Ratio Cu:Ni	Layers of each		Ultimate Tensile Strength
	per cm.	per in.	2950 kg./cm.[2]
5:1	68	170	42,000 lb./sq. in.

and of nickel, have a much higher tensile strength than has the copper alone.[1] This process has been made the basis for the electrolytic reproduction of engraved printing plates at the U. S. Bureau of Engraving and Printing.[2]

A somewhat similar effect is produced if two metals are deposited simultaneously as an alloy, *e.g.*, in brass plating or in

[1] BLUM, W., *Trans. Am. Electrochem. Soc.*, vol. 40, p. 137, 1921, and *Chem. Met. Eng.*, vol. 25, p. 961, 1921.

[2] BLUM, W., and SLATTERY, T. F., *Chem. Met. Eng.*, vol. 25, p. 320, 1921.

the deposition of lead-tin alloys. In general, such alloys have a much finer structure than either of the component metals deposited separately under similar conditions. In a certain sense, therefore, each metal acts as an addition agent with respect to the other, in that each metal prevents the growth of the crystals of the other.

All of the above cases point to the probability that the general effect of colloids is that of preventing continuous growth of individual crystals, and of producing thereby a uniform distribution of the current upon the cathode.

Among the causes which normally promote the production of rough or treed deposits is the presence of suspended particles, especially conducting particles of metal, carbon, etc., derived from the anodes. Such particles lodge upon the cathodes and serve as nuclei for the growth of large crystals or of trees.[1] In continuously filtered solutions very much smoother deposits can be obtained. If, now, addition agents are added to such clear solutions, it is found that they have less effect upon the deposits than they have in unfiltered solutions; in other words, much of the effect of addition agents in reducing roughness is that of counteracting the influence of suspended particles. On the other hand the filtration of solutions containing colloidal addition agents may almost entirely remove such substances, which must then be replenished.

The effect of inorganic addition agents such as aluminum sulphate in zinc baths, has been found by Thompson[2] to be due largely to their buffer action. Aluminum salts hydrolyze and precipitate aluminum hydroxide at a pH of about 5, and thus prevent the solution from becoming less acid until all the aluminum has been precipitated. The appearance of a white gelatinous precipitate in such solutions also serves as an indication of the need for more acid. Thompson was unable to detect a trace of aluminum in the deposited zinc.

The effect of crystalloidal organic agents is still less subject to generalization and much work must be done before any clear relation can be established between the structure of organic compounds and their effect upon metal deposition. Organic

[1] This behavior is well illustrated for nickel deposits in a paper by Upthegrove, C. and Baker, E. M., *Trans. Am. Electrochem. Soc.*, vol. 53, p. 389, 1928.

[2] *Trans. Am Electrochem. Soc.*, vol. 50, p. 193, 1926.

compounds, such as tartrates, citrates, and acetates, or the corresponding acids, are probably useful in forming complex ions and also in preventing the precipitation of hydroxides or basic salts.

In many cases reducing substances probably act as addition agents through the production of colloids, either organic colloids or colloidal particles of the metal. In extensive experiments upon the electrochemical equivalent of silver, conducted at the Bureau of Standards,[1] it was found that the presence of very minute amounts of both inorganic and organic reducing substances, such as hydroxylamine, aldehydes, phenol, hydroquinone, etc., had the same general effect, *viz.*, a diminution in the size of the crystals and the formation of striations. The extensive studies of Mathers[2] and his students upon addition agents in lead baths emphasize the fact that to a great extent the effects of addition agents are specific. With our present knowledge it is impossible to predict the exact influence of any addition agent in any particular solution.

In the illustrative experiments at the Bureau of Standards, a few deposits were produced from solutions containing respectively glue and glucose, selected as typical colloidal and reducing substances. As above explained, however, it is at least probable that the glucose may have produced or fostered the formation of colloids, or that it contained an appreciable amount of dextrin, which is a colloid. The results shown in Fig. 19 are interesting simply as an illustration of the magnitude of the effects produced. In general, it has been observed that deposits formed in the presence of addition agents are fine-grained and hard, but unfortunately they have a tendency to be brittle and are therefore not always satisfactory for electroplating or for electroforming. Another consideration which has retarded the more general use of addition agents is the difficulty of controlling such solutions by any known analytical methods. This is illustrated by the fact that a very marked effect is produced upon copper deposits by the presence in the solution of a few parts per million of glue, a concentration entirely outside the limits of present analytical procedures. The polarization box (p. 72) has been used in a few plants for measuring the effective concentration of

[1] Rosa, E. B., Vinal, G. W., and McDaniel, A. S., Bureau of Standards, *Scientific Paper* 195, 1912.

[2] *Trans. Am. Electrochem. Soc.*, vol. 21, p. 313, 1912; vol. 24, p. 117, 1914; vol. 27, p. 131, 1915.

glue in copper and lead refining solution. Within certain limits the cathode polarization (for otherwise uniform conditions) depends upon the concentration of glue present.

Whenever substances which may be employed in relatively high concentrations, and which are susceptible of estimation by analysis, are applicable, their use is preferable. Even here,

b

FIG. 19.
20 diam.
Copper Deposits.
Effect of "Addition Agents."
a "Standard" solution.
b " " + glue.
c " " + glucose.

however, the formation of secondary products may lead to unsatisfactory deposits. With the present limited knowledge of addition agents, they are less useful in electroplating than in electrorefining, in which latter industry they have been extensively applied.

8. STRUCTURE OF BASE METAL

No discussion of the structure of electrodeposits is complete that omits reference to the very important effect of the structure of the base metal. This relation was clearly demonstrated by one of the authors (G. B. Hogaboom) in an address to the American Electroplaters' Society in July, 1921. He cited numerous instances in which defective plating could be traced very directly to an abnormal or undesirable structure of the steel or brass used in the base metal. In recent experiments[1]

[1] BLUM, W., and RAWDON, H. S., The influence of the base metal on the structure of electrodeposits, *Trans. Am. Electrochem. Soc.*, vol. 44, p. 305, 1923.

GRAHAM, A. K., Some relations between the microstructure of metal surfaces and deposits made thereon, *Trans. Am. Electrochem. Soc.*, vol. 44, p. 427, 1923.

illustrated in Fig. 20, it has been shown that when copper is deposited from the sulphate bath upon either cast or rolled copper which has been cleaned with nitric acid, the deposited metal consists of crystals which are extensions of the crystals present in the base metal. This subject deserves careful investigation by those engaged in the metal industries.

9. METAL DISTRIBUTION AND THROWING POWER

In both electroplating and electroforming it is important to know not only the structure of the coating, but also its relative thickness on different parts of the cathode, especially if the latter is of irregular shape or is deeply recessed. The principles which determine the current and metal distribution have been investigated at the Bureau of Standards.[1] The conclusions may be summarized as follows:

Usually, in electroplating and electroforming, a definite minimum thickness of metal is required either for appearance, protection, or service. The effort to secure the most nearly uniform distribution of metal over the entire cathode surface therefore depends upon depositing as little metal as possible on the rest of the object, while producing this minimum thickness upon the least accessible part.

When any irregularly shaped article is made the cathode in a plating bath, certain parts are nearer to the anode than others, and hence will naturally receive higher current densities. Suppose that in any given case the resistance from the anode to the far point on the cathode is five times as great as to the near part. Then, according to Ohm's law, the current density on the near part would be five times as great as on the far part. Such a distribution, which exists only when there is no polarization at the cathode (*e.g.*, when a high-frequency alternating current is used), is known as the "primary current distribution." It is determined solely by the size, shape, and position of the anodes and cathodes and of the bath, and does not depend upon the solution used.

As explained on page 72, when metal is deposited the solution close to the cathode tends to become depleted in metal and in

[1] HARING, H. E., and BLUM, W., Current distribution and throwing power in electrodeposition, *Trans. Am. Electrochem. Soc.*, vol. 43, p. 303, 1923; and HARING, H. E., Throwing power, cathode potentials and efficiencies in nickel deposition. *Trans. Am. Electrochem. Soc.*, vol. 46, p. 107, 1924.

FIG. 20.—Section of the Chilled Side of a "Pig" of Cast Copper, upon Which Copper Was Electrolytically Deposited. ×100.

a, the surface was cleaned but not pickled, prior to the electrodeposition.

b, the surface was pickled after cleaning.

The various zones indicated in "b" are the same throughout all of the micrographs: w, base metal; x, electrodeposited copper (first layer); y, electrodeposited nickel; z, electrodeposited copper (second layer).

metal ions. Naturally a higher potential is required to deposit metal from a dilute than from a concentrated solution; in other words, a "concentration polarization" is produced. Usually this polarization is greater for high than for low current densities. In consequence, the current density at the near point is less than it would be if there were no polarization, and the current distribution becomes more nearly uniform than the primary distribution, *e.g.*, 4.5 to 1, instead of 5 to 1. The "secondary" current distribution is that which is actually produced, and is always more nearly uniform than the primary distribution.

In solutions of metals which stand below hydrogen in the electromotive series (Table 10), the cathode efficiency decreases as the current density is increased, hence there is relatively more hydrogen and less metal deposited at high than at low current densities. In consequence, the "metal distribution" is often more nearly uniform than the actual or secondary current distribution, *e.g.*, it may be 4 to 1, instead of 4.5 to 1.

The plater commonly attributes to solutions which produce relatively uniform metal distribution "good throwing power," which term, however, is not usually defined explicitly. For comparative purposes, the throwing power may be defined as "the improvement in per cent, of the metal distribution ratio, above the primary current distribution ratio." Thus, if in the above illustration the primary ratio is 5 to 1, and the metal ratio is 4 to 1, the throwing power is + 20 per cent, which is the percentage improvement in the distribution ratio. This is equivalent, in a simple case, to the statement that while depositing the required thickness of metal on the least accessible part, 20 per cent less metal will be deposited on the near part than if there were no throwing power.

If, as may occur, the metal ratio should be 6 to 1, the solution would possess a *negative* throwing power, in this case −20 per cent. This condition exists in many nickel plating solutions, and almost invariably in chromium plating baths. A negative throwing power is always associated with a lower cathode efficiency at a low current density than at a higher current density.

The factors which determine the throwing power under any given conditions are: (*a*) the degree to which the polarization increases with increased current density, (*b*) the conductivity of the solution, and (*c*) the cathode efficiencies at the respective current densities. If for any solution the cathode single poten-

tial is plotted against the current density, curves such as those shown in Fig. 21 are obtained. These curves may be divided roughly into three classes: (*a*) Those, such as for mercury and lead, which are nearly vertical, *i.e.*, in which there is almost no polarization. Such solutions have almost no throwing power. (*b*) Those, such as for copper sulphate, nickel sulphate, and zinc sulphate, which are inclined slightly, especially at low current densities. These solutions have moderate throwing power. (*c*) Those for complex solutions, such as the copper and zinc cyanides. These are very much inclined, *i.e.*, there is marked polarization and consequently these solutions have very good throwing power.

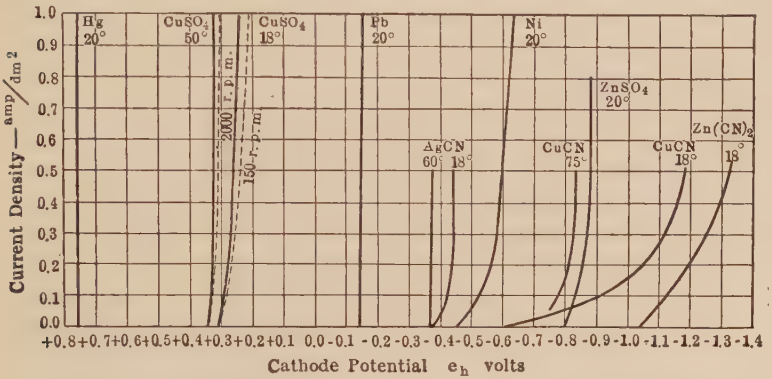


FIG. 21.—Current Density-Cathode Potential Curves. Derived from Foerster "Elektrochemie Wässeriger Lösungen." 3rd Edition. 1922.

Throwing power may be improved by (1) causing the cathode polarization to increase more rapidly with an increase in current density (*i.e.* by making the polarization curve more inclined); (2) increasing the conductivity; or (3) making the cathode efficiencies at low current densities more nearly equal to those at higher current densities.

The total drop in potential between the anode and the two parts of the cathode must be equal. If, however, the polarization is greater upon the near than upon the far point, this is equivalent to an increased resistance to the near point. The lower the primary resistance to the near point (*i.e.*, the better the conductivity of the solution), the greater will be the relative effect of the polarization. An increase in conductivity will not, however, improve the throwing power unless there is appreciable

polarization. Any given change in operating conditions may produce opposite effects upon the three factors, and the actual result will depend upon which effect predominates. Thus, *e.g.*, warming a solution increases the conductivity but decreases the polarization. The latter effect is usually more pronounced, hence an elevation in temperature generally decreases throwing power.

The above principles may be illustrated by the results obtained with acid copper solutions in a simple apparatus shown in Fig. 22. In the form that is now in general use this consists of a hard

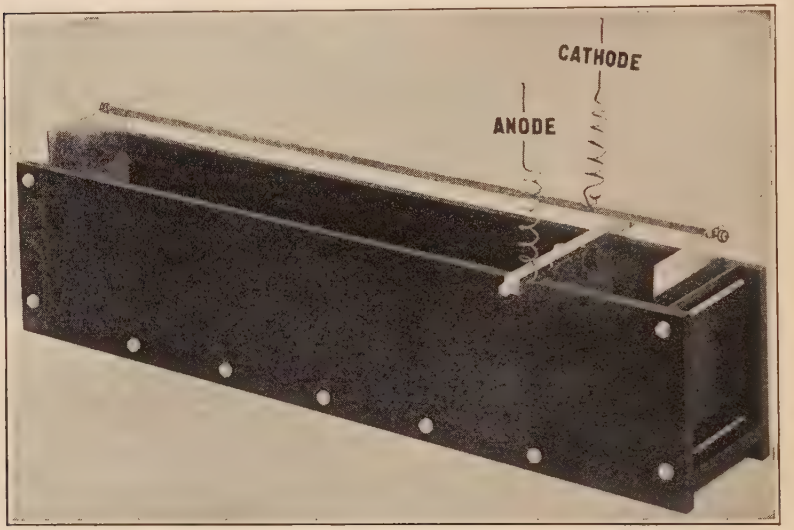


Fig. 22.—Box Used to Measure Throwing Power.

rubber box[1] in which two plates, each having an exposed area 5 × 5 cm. (2 × 2 in.), are placed at definite distances, *e.g.* 2.5 and 12.5 cm. (1 and 5 in.) from a gauze anode. The two plates *n* and *f* are connected with a heavy brass rod, and therefore represent the two parts of any object such as that considered in the above discussion. In the original experiments, made in a larger box, 60 cm. (24 in) long, and with plates 10 × 10 cm. (4 × 4 in.), the following conditions were employed as a "standard" for purposes of comparison:

[1] By the use of appropriate slots, the same box may be used for approximate measurements of polarization (p. 72) resistivity (p. 77) and throwing power.

Composition of Solution	N	g./l.	oz./gal
$CuSO_4.5H_2O$	1.5	187	25
H_2SO_4	1.5	73	10

Temperature: 21°C. (70°F.)
Total current 2 amp. on 2 sq. dm. (equivalent to an average current density of 1 amp./dm.^{2}, or 9.3 amp./sq. ft.)
Primary current ratio = 5:1

Under these conditions the throwing power was 9.4 per cent.[1] Variation of the above conditions yielded the following results:

(*a*) *Current Density.*—An increase in the total current to 4 amp. (*i.e.*, in the average current density to 2 amp./dm.^{2}, or 18.6 amp./sq. ft.) decreased the throwing power to 7.4 per cent. An increase in current density decreases the throwing power if the latter is due principally to the polarization.

(*b*) *Temperature.*—An elevation in temperature to 45°C. (113°F.) decreased the throwing power to 2.2 per cent.

(*c*) *Agitation.*—Stirring the solution with air, as is done in electrotyping, decreased the throwing power to 3.4 per cent. In certain cases, however, a slight degree of agitation may prevent "pocketing" of the solutions in the recesses and thus improve throwing power.

(*d*) *Metal Salt Concentration.*—An increase in the copper sulphate content to 2 N (249 g./l., or 34 oz./gal.) decreased the throwing power to 7.2 per cent, a natural result of increasing the supply of copper salt and copper ions.

(*e*) *Acid Concentration.*—Increasing the sulphuric acid content to 2 N (98 g./l., or 13 oz./gal.) increased the throwing power to 10.8 per cent; and decreasing the acidity to 0.5 N (25 g./l., or 3.3 oz./gal.) reduced the throwing power to 4 per cent. The effect of the acidity is due principally to the change in conductivity.

(*f*) *Addition Agents.*—Neither aluminum sulphate nor dextrose produced any appreciable effect on throwing power. Colloidal substances, such as dextrin and gelatin, increased the throwing power to 12 and 18 per cent respectively. These results are probably due to the increased viscosity of the cathode film, and to the greater cathode polarization caused thereby.

[1] These results are not equal numerically to those that would be obtained with a smaller box. The relative results and conclusions in comparable experiments are however similar.

In the above investigation a few experiments with a cyanide copper solution showed that its throwing power is high, *i.e.*, about 40 per cent, which corresponds with the general observations of platers. This increase in throwing power is due principally to the greater cathode polarization in cyanide solutions, and partly to the relatively low cathode efficiency at high current densities.

As defined here, throwing power is a property of the plating solution under the specified operating conditions, and expresses the relation between the primary current distribution and the actual metal distribution. In all cases, and especially when the throwing power is poor, as in chromium plating, it is desirable to make the primary distribution as uniform as possible. This depends upon the shape of the article and its position in the tank with respect to the anodes and other equipment. As it is not generally possible to change the shape of the article to be plated, attention must be paid to its position in the bath. Ingenuity in thus improving the current distribution in chromium plating largely accounts for its present successful operation in spite of the poor throwing power. Among the practical methods of improving the current distribution are the following:

(*a*) Make the anodes and cathodes as nearly parallel or concentric as possible, *e.g.*, by the use of inside anodes in reflectors, tubes, etc.

(*b*) Increase the average distance from the anodes to the cathodes, and thus make the relative distances to the near and far points more nearly equal.

(*c*) Rack the work in such a way that parts likely to get an excessive current density, such as projecting points, are relatively close to a conducting part of the rack, or of a wire cage surrounding the point. The wire acts as a thief and "steals" the current from the adjacent parts of the cathodes.

(*d*) Shield projecting parts by some insulating part of the frame, such as a strip of glass, bakelite, etc.

By applying one or more of the above procedures, it is frequently possible to plate articles of quite complicated shapes, even when the throwing power of the solution is poor.

10. SUMMARY

From a consideration of the various factors discussed in this chapter it is possible to derive certain general principles which

may determine the choice in the selection of operating conditions. Even if such conclusions are at present only qualitative and approximate they may be suggestive and may lead to the acquisition of more definite information. It should be emphasized, however, that there are still many conditions and experiences in plating that cannot be explained by the above or any other principles now known.

In the choice of the metal salt, the effort should be made to secure a substance which has, or the solution of which has, as many as possible of the following properties. By the "metal salt" is meant that compound which contains the major part of the metal to be deposited, regardless of whether the salt is purchased as such, *e.g.*, copper sulphate and zinc chloride, or whether it is produced in the solution, *e.g.*, sodium silver cyanide and lead fluoborate.

(*a*) High solubility in order to yield a high metal concentration.

(*b*) Good conductivity.

(*c*) Stability, *i.e.*, resistance to hydrolysis (formation of basic salts) and to oxidation or reduction.

(*d*) A low metal ion concentration, such as is possessed by complex cyanides.

(*e*) The ability to dissolve the anode nearly quantitatively. This is required especially for metals such as nickel which have a tendency toward anode passivity.

(*f*) Good throwing power. In certain cases the conditions that will produce good throwing power are such as to decrease the average rate of deposition, or to increase the required voltage. Whether in any given operation the conditions for securing high throwing power and more uniform metal distribution are desirable, must be determined by economic considerations, such as the relative cost of the metal and of the time and labor involved.

(*g*) A sufficiently low price to permit economic operation in the light of its relative advantages.

Since no single substance has in a high degree all the properties just listed, it is frequently necessary to add other substances to the solutions. While such additions are entirely justifiable when their use has proved beneficial, it cannot be too strongly emphasized that the simplest successful solutions should be employed, both to avoid complicated reactions and to facilitate analysis of the solutions. Wherever it is possible to employ a single substance to accomplish two or more purposes,

the single substance should be used rather than two separate substances. In this connection, those materials which may be formed in preparing the solution of the major metal salt are just as truly additions as if they had been intentionally introduced. Thus if silver chloride is used in making a solution of sodium silver cyanide, the sodium chloride simultaneously produced may have its effect on the properties of the solution. The fact that a further addition of the substance produces no noticeable effect is no evidence that the original amount is without effect. Thus the fact that increasing the sulphuric acid in a copper solution from 0.5 *N* to *N* has little influence does not show that the 0.5 *N* originally present is without effect. Among the purposes for which substances may properly be added to plating solutions are the following:

(*a*) To increase the solubility either of the metal salt or of the oxides or basic compounds that may be formed. Thus the presence of sulphuric acid in a copper sulphate solution prevents the formation of basic cupric or insoluble cuprous compounds. Similarly the presence of excess cyanide prevents the precipitation of insoluble cyanides.

(*b*) To increase the conductivity. This may be accomplished by the addition of an acid to acid solutions, such as copper sulphate, of a base to alkaline or cyanide solutions, and of a well-conducting salt to solutions which must be kept nearly neutral.

(*c*) To regulate the acidity or, more specifically, the hydrogen ion concentration of such plating solutions as zinc and nickel, which must not have excessive acidity. For this purpose weak acids (or their salts) may be used, such as acetic and boric acids.

(*d*) To reduce the metal ion concentration. In the case of simple solutions this may be effected by the addition of a salt with a common ion, *e.g.*, sodium or magnesium sulphate to nickel sulphate solutions. If we consider a complex salt, such as a double cyanide, as the major compound, it already has a low metal ion concentration which can be further reduced by the addition of an excess of cyanide. In general a decrease in metal ion concentration causes an increase in cathode polarization.

(*e*) To aid anode solution and decrease the anode poalrization, for example, the addition of nickel chloride or alkali chlorides to a nickel sulphate solution and the addition of cyanides to an alkaline zinc solution.

(*f*) To increase the throwing power. Most conducting salts and addition agents and other substances that increase cathode polarization, tend to improve this property.

(*g*) To form colloids which will migrate to the cathode and reduce the size of the crystals. These may be added directly in the form of glue, gelatin, casein, albumen, etc., or in the form of substances which will yield colloids by hydrolysis or reducing action.

(*h*) To exert a reducing action at the cathode or in the solution. This may possibly be associated with (*g*).

The *current density* that may be employed will depend upon the composition and temperature of the solution and upon the nature of the metal to be deposited, the degree of agitation, and the composition and size of the anodes. In general, if fine-grained deposits are desired, the highest current density should be employed which will not produce "burnt" or "cracked" deposits. If coarse or soft deposits are desired, low current densities should be used.

A relatively low *temperature* should be maintained if fine-grained dense deposits are desired, and vice versa. If, however, high current densities are used at elevated temperatures, the effect of increased current density may counterbalance that of temperature, and fine-grained deposits may be secured. For nickel, chromium, iron, and other metals likely to absorb hydrogen, less brittle deposits are obtained in warm than in cold solutions. The temperature selected should be kept constant, for example by thermoregulators, such as are now commonly used for chromium plating.

Whenever feasible, the solution should be *agitated* or at least circulated, or the cathodes should be moved during the deposition. Under such conditions frequent or continuous filtration of the solutions is advantageous.

CHAPTER VIII

THE SELECTION, SPECIFICATION, AND INSPECTION OF ELECTRODEPOSITS

1. CHOICE OF METAL COATINGS

As electroplating is used to a great extent for ornamental purposes, it might at first appear that the color and luster are the principal factors which determine the choice of the metal to be deposited. Since, however, even ornamental coatings must possess reasonable resistance to tarnish or corrosion, and must in some degree protect the underlying or base metal, the ultimate factor in the proper choice is the chemical behavior of the metals. The ability of any metal to resist corrosion, or to protect any other metal against corrosion, is determined primarily by its position in the electrochemical series (page 68). As there indicated, those metals which are highest in the series, *i.e.*, have the most negative single potentials, possess the greatest solution tension, or the greatest tendency to corrode. By virtue of this fact, when such metals are in intimate contact with metals lower in the series, they protect the latter metals from corrosion. The most common and most important application of this principle is the widespread use of zinc and cadmium coatings for protecting iron or steel against rusting. It has been frequently shown that appreciable areas of iron may be exposed without rusting, provided a zinc or cadmium coating is adjacent to the iron.

The electrochemical position of the metals is, however, only an index of their relative initial tendency to corrode. Other factors may determine the actual behavior of any particular metal. Thus, *e.g.*, if a metal tends to become "passive" (page 73), it may resist corrosion better than metals lower in the series. This property of passivity accounts for the very marked tendency of nickel to remain bright and for its consequent use in plating. Simply from their positions in the series we would expect nickel to corrode more readily than copper, but, as is well known, nickel

will remain bright much longer than will copper under ordinary atmospheric conditions. The resistance of chromium under many conditions of exposure is due to its passivity. In general when a metal coating is passive, it tends to accelerate the corrosion of the base metal.

Other factors which influence the corrosion of any metal are the solubility and physical properties of the products of oxidation or corrosion. From their relative positions we might think that aluminum would corrode much more readily than zinc. Actually, aluminum is more resistant to corrosion, probably because the aluminum oxide formed is less soluble and more dense than the zinc oxide (or carbonate) formed by corrosion. The resistance of aluminum to corrosion is usually attributed to the presence of a very thin film of oxide.[1] It is probably because aluminum does not corrode readily and because it becomes coated with a film of oxide and thereby electrically insulated, that a coating of aluminum does not exert as much protection to steel as does a coating of zinc. It is important, therefore, to bear in mind that the electrochemical series is simply a guide to the proper selection of metals, and that other factors must also be considered.[2]

The very extensive use of iron and steel, together with the fact that unless protected they rust when exposed, had led to numerous investigations concerning the causes and prevention of such corrosion. Whatever may be the ultimate solution of this problem, it is obvious that at present iron must be protected if it is to have any extended service. During the war there was a great demand for information on methods of protecting iron, and many tests and investigations were carried out in various laboratories.[3] The net result of these and earlier studies, and of field observations, was that, of all commercial metallic coatings then in common use, zinc furnished the best protection to iron against the atmospheric agencies. It was

[1] In recent years a process has been developed in England for protecting aluminum and its alloys against corrosion by producing an oxide film by anodic treatment in dilute chromic acid.

[2] A more detailed description of the preparation, value and testing of coated metals is contained in "Protective Metallic Coatings" by RAWDON, H. S., *A. C. S. monograph* 40, Chemical Catalogue Co., 1928.

[3] The general results and conclusions of this work are published in Circular 80 of the Bureau of Standards, upon "Protective Metallic Coatings for the Rustproofing of Iron and Steel."

therefore very extensively used upon military supplies, including boosters and adapters for shells, hardware for ammunition boxes, parts for airplanes, marine fittings, etc.

(a) **Value of Zinc Coatings.**—In general it is found that a given weight or average thickness of zinc yields about the same protection whether it has been applied by hot dipping, sherardizing, or electroplating (so-called "electrogalvanizing"), in either the sulphate or cyanide bath. Zinc plating is especially useful for small articles, including threaded or dimensioned parts, since the average thickness of the zinc can in this process be controlled approximately by the current density and time of deposition.

From the experience obtained, it appears very desirable that zinc plating should be applied much more extensively in industry than at present. In general, it may be stated that wherever iron or steel is exposed to outdoor corrosion, and when appearance is not a primary consideration, zinc or cadmium coatings should be given preference. Unfortunately, the opinion still prevails that because copper itself is fairly resistant to corrosion, it must protect iron; whereas its presence may actually accelerate corrosion of the iron. In the airplane industry the use of copper plating has been superseded by zinc, and to some extent by cadmium.

Unfortunately, zinc coatings do not possess or retain a pleasing appearance, and in consequence for many purposes they are not acceptable. Various methods have been suggested to secure the protective value of zinc and a more ornamental finish. Zinc plating followed by nickel plating has been frequently employed, in some cases with fair success, but in general such a combination cannot be recommended. Years ago it was shown[1] that the protective value of zinc coatings is reduced by contact with nickel or any metal lower in the electrochemical series than zinc; and that if the zinc is exposed either through initial porosity or subsequent abrasion of the nickel, the zinc will corrode and will tend to cause peeling of the nickel. The use of a copper strike preparatory to zinc plating is objectionable because the presence of the copper accelerates corrosion of the zinc and subsequently of the underlying steel. The maximum

[1] WATTS, O. P., and DE VERTER, P. L., The protection of iron by electroplating, *Trans. Am. Electrochem. Soc.*, vol. 30, p. 145, 1916.

protective value of zinc is therefore afforded when it is applied directly to the iron and is not coated with any other metal.

Probably the most satisfactory method for treating zinc plating to produce a desirable appearance is by the application of either air-drying or baking enamels or japans. It is well known that paints or enamels do not adhere well to zinc coatings produced by hot dipping, although no satisfactory explanation for this behavior has been offered. The remedy frequently employed, *viz.*, treatment of the zinc surface with a weak acid or a solution of a copper salt, is at best a makeshift, since the thickness and protective value of the zinc coating may be thereby materially reduced. With zinc plated coatings, however, there is usually very little difficulty in securing good adherence of most paints or enamels, although with some paints poor results are obtained. In a few cases also a tendency has been observed for the paint or enamel film to become brittle when in contact with zinc. This subject is in need of investigation. In most cases fairly satisfactory adherence can be secured by the following procedure. The zinc plated articles are heated for a short time to the temperature to be used in the enameling ovens, in order to expel any occluded gases or moisture which might otherwise produce blisters. They are then coated with a metal primer, and subsequently with an enamel or japan especially developed for this purpose, and baked in the usual way. Such a procedure not only produces a desired color or finish, but also adds materially to the service of the coating, since the zinc is preserved until the enamel is abraded, after which the zinc exerts its normal protective action.

(b) **Value of Cadmium Plating.**—The recent activities toward the development and application of cadmium plating may be considered as an effort to secure, by the use of this element, in as high a degree as possible, the protective value of zinc and the pleasing appearance of nickel. Cadmium plating is now carried out commerically with uniform success and there is a distinct field for its use. It will be noted in Table 10 in the Appendix that the potential of cadmium is indicated as uncertain, at least the relative positions of cadmium and iron are in question. Unless cadmium is above iron in the series, it would not be expected to protect exposed iron against corrosion. From its position in the periodic system, and its general chemical and electrochemical behavior, it is believed that it is correctly placed

above iron, even though the present numerical values are in the reverse order. That it does protect exposed iron against corrosion, especially in a salt solution or salt spray, has been shown by Blassett[1] and others, and also by tests made at the Bureau of Standards. As, however, its potential is very close to iron, it cannot afford as much *intrinsic* protection as zinc; in other words, it will probably not protect so large an exposed area as will a similar zinc coating. It follows, therefore, that, to a greater degree than with zinc, it is essential that cadmium coatings must be nearly impervious in order to furnish continued protection.

On the other hand, the cadmium coating will not itself corrode so rapidly as will zinc under most conditions, and hence the cadmium coating will preserve a better appearance and in the salt spray a given thickness of cadmium will protect the steel longer than will the zinc. Data obtained by the U. S. Air Service indicate that a cadmium coating is equal in protective value to one of zinc that is three times as thick. Cadmium has been found especially useful for marine exposure.

As the potential of cadmium is relatively close not only to iron but also to nickel, it is easier to nickel plate over cadmium coatings than over zinc, and there is less tendency for the cadmium to cause deposition of nickel by immersion. If the cadmium coating is subsequently exposed by abrasion or porosity, there is tendency for it to corrode and to cause peeling of the nickel. In the salt spray or atmospheric exposure the nickel accelerates the corrosion of the cadmium and makes the protection less than that of cadmium alone, though slightly better than that with nickel alone.

(c) **Value of Nickel Plating.**—It must be recognized, however, that for many purposes it is desirable to employ coatings with a bright metallic luster. For such cases nickel has hitherto been considered superior to any other metal, but the recent developments in chromium plating have shown that for tarnish resistance chromium is far better than nickel. As however, when chromium plating is applied to steel for protection and ornament, it is almost invariably preceded by a nickel coating, it is just as important as ever to be able to employ nickel deposits that furnish good protection against corrosion.

[1] *Metal Ind.*, vol. 9, p. 509, 1911.

From an extensive study of the latter subject[1] it was concluded that the production of protective nickel deposits depends upon making them as nearly impervious as possible. Under most conditions of exposure including even a salt spray, the nickel itself is attacked but slightly if at all. Failure is caused by the corrosion of iron that is exposed through pores in the coating. None of the methods that depend upon special pickling of the steel before plating or upon special constituents of the nickel bath was found by the above authors to make sufficient improvement to yield thin nickel deposits (less than 0.0005 in. or 0.013 mm.) that were nearly impervious. (Recent commercial experience indicates that in some cases electrolytic cathode pickling of steel has decreased the porosity and increased the adhesion of the nickel.) The only method that produced any marked decrease in porosity and increase in protective action was to make the nickel (or composite) coating relatively thick, preferably not less than 0.001 in. (0.025 mm.). The presence of appreciable amounts of iron in the nickel deposits greatly decreased their protective value.

The application of a fairly thick deposit of copper from a cyanide solution (*e.g.* 0.0003 in. or 0.008 mm.) prior to nickel plating, decidedly increases the protective value, but a thin flash of copper, such as was formerly used extensively before nickel plating, has little value and may actually accelerate the corrosion. Best protection is obtained from composite coatings, consisting, *e.g.*, of successive layers of nickel, copper and nickel, with a total thickness of at least 0.001 in. (0.025 mm.). Practical experience indicates that if the copper coating is buffed before the application of the final nickel, the protective value is increased. Such deposits are now in general use on bumper bars and radiator shells, including those that are subsequently chromium plated.

(d) **Value of Chromium Plating.**—The recent phenomenal interest in chromium plating, and the many applications in which it has proven successful, have quite naturally led to some misconception and consequent disappointments. It is well therefore to discuss in some detail those properties of electrodeposited chromium which determine or limit its usefulness.

The two outstanding properties of chromium that have caused its present popularity are its extreme hardness and its resistance

[1] Thomas, C. T. and Blum, W., *Trans. Am. Electrochem. Soc.*, vol. 48, p. 69, 1925; and vol. 52, p. 271, 1927.

to tarnish and to corrosion under many conditions. Its great hardness has led to many applications upon mechanical equipment such as gages, dies and mandrels, and upon electrotypes and other printing plates, or to other uses where resistance to wear and abrasion is important.[1] It is not possible to give exact ratios of service, but tests with gages indicate that the chromium resists wear from two to five times as long as any steel. On printing plates it lasts about twice as long as case-hardened steel, and about four times as long as a nickel surface. Another advantage of chromium on wearing surfaces such as printing plates, is that when the chromium coating is partly worn off, it can be entirely removed by stripping and a new deposit applied.

One reason that the service of chromium surfaces can not be exactly predicted, is that the hardness varies with the conditions of deposition. Some tests indicate that the hardest deposits are obtained when the deposit is just slightly "frosted," *i.e.*, the current density is as high as possible without actually burning. In general when chromium is used for wear resistance, it is deposited directly upon the base metal, which is usually steel.

The application of chromium for such uses as upon the exterior of automobiles depends principally upon its resistance to tarnish under most atmospheric conditions. This is due (p. 73) to the passivity of chromium. As indicated in Table 10, (appendix) the position of chromium in the electrochemical series is such as to make it similar to zinc in properties. In the active state it is very much like zinc, *e.g.*, it dissolves readily in hydrochloric acid. This fact had led occasionally to the erroneous statement that chromium will protect exposed steel against corrosion, just as do zinc and cadmium. Such protection is impossible however if the chromium itself stays bright, as it does under most conditions. If the conditions were such that the chromium did protect exposed iron, the chromium would necessarily have lost its valuable property of tarnish resistance.

Chromium coatings, especially when thin, are not usually impervious. In addition to having such porosity as is present in most other plated coatings, chromium has a tendency to develop hair-line cracks, especially when the thickness is somewhat greater than 0.00004 in. (0.001 mm.). Much thicker deposits, *e.g.*, 0.001 in. (0.025 mm.) of chromium may still have such

[1] Blum, W., Mechanical applications of chromium plating, *Mech. Eng.* vol. 50, p. 927, 1928.

cracks, but they have during deposition, become sealed over to such an extent that the deposits are more nearly impervious. To deposit thick coatings of chromium requires considerable time and electricity and is expensive. Moreover thick deposits of chromium are more brittle than thinner coatings.

When it is desirable to protect iron and steel against corrosion and to have a chromium surface to resist tarnish, *e.g.*, on automobile radiators and bumpers, the most practical way is to plate the steel with thick coatings of copper and nickel (p. 125) and to then apply to the polished nickel a thin coating of chromium, *e.g.*, 0.00002 to 0.00004 in. (0.0005 to 0.001 mm.). The fact that such thin coatings of chromium not only greatly increase the tarnish resistance, but also materially retard the corrosion of the steel, is most probably due to the fact that chromium surfaces are not readily wet by water or most liquids. Hence there is less tendency for moisture to be retained on the chromium, or to be drawn into capillary pores.

Other properties of chromium which may determine or limit its value for a given purpose are its thermal expansivity, electrical conductivity, and reflecting power. The coefficient of expansion of chromium is about 8 parts per million per degree Centigrade, (8×10^{-6}), which is about the same as that of platinum and ordinary glass, but much lower that that of most metals. Therefore when chromium is plated upon steel or brass and heated to high temperatures, there is a tendency for the chromium to flake off. This tendency is less for cast iron, which has a lower expansion coefficient than steel. This fact favors the use of chromium on cast-iron bottle molds that are exposed to high temperatures.

While chromium is a good conductor of electricity, it does not readily make close contacts with other metals, and where a low resistance contact is desired the chromium plating is not so good as gold plating.

The reflecting power of chromium is about 70 per cent in the visible spectrum, as compared with about 90 per cent for silver and about 60 per cent for nickel. As however, chromium preserves its luster much better than does silver, its permanent reflecting power may be much better than that of silver. It is especially useful on locomotive headlights, or other reflectors exposed to sulphur compounds. The reflecting power of chromium for ultra-violet rays is better than that of any other metals

except aluminum. As it preserves a higher luster than aluminum, chromium is very useful on reflectors used for ultra-violet rays, *e.g.*, for therapeutic purposes.

The coefficient of friction of chromium in contact with other metals and a lubricant is relatively low and constant. In some cases chromium has proved valuable upon bearing surfaces.

The selection of electrodeposited metals for other purposes is often determined by their specific properties, *e.g.*, gold for its appearance and its resistance to tarnish; silver for its high reflecting power and its resistance to the action of most foods; copper in electrotyping because of its ease of deposition; nickel, cobalt, iron and chromium on printing plates because of their relative hardness; lead for its resistance to the action of certain chemicals; tin for its resistance to foods, etc. Consideration of the specific requirements for each class of work indicates that there are still great possibilities for improvement which may be brought about either by changes in existing processes, or by the application of at present rare or unused metals.

2. PROPERTIES OF ELECTRODEPOSITS

Having decided upon the metal to be deposited, it is desirable to fix upon some basis of quality for the product. The criteria of a satisfactory deposit depend upon the purpose to be served, and also in some measure upon the point of view, whether that of the manufacturer or of the consumer. All angles must be considered if a permanently satisfactory basis is to be reached. It is possible to define the quality of an electrodeposit either in terms of the process to be employed or of the requirements to be met. Unfortunately, neither basis of specification is entirely satisfactory. In all too many plating plants today the conditions and facilities are not such as to permit that definition and control of the various factors which are necessary to insure a uniform product, although there has been a marked improvement in this respect in recent years. Moreover, the fixing of process details, especially in formal specifications, is undesirable since it tends to take away from the operator the initiative and responsibility which are essential to progress. On the other hand, the factors which determine the service of the product are usually not well understood, and even when tentative specifications are prepared, methods of testing are often inadequate or even entirely lacking. There is today no greater need in the plating industry

than the development of reliable specifications and methods of testing the products. During the war, in the purchase of military supplies, much confusion and delay was often caused by the absence of acceptable standards, or by the specification of process details which were in some cases entirely inoperable. The following pages will serve to emphasize rather than to fill the above need and perhaps to point out possibilities for research.

Among the various factors which may determine the usefulness or durability of any electrodeposited metal are the thickness, distribution, permeability, adhesion, and hardness. Few, if any, of these properties can be measured directly.

(a) **Thickness.**—For many metals it is possible to determine, by some stripping method, the total weight of metal coating upon a given area; and from this to calculate the *average thickness* of the deposit. Such information is often useful, especially in the case of more valuable metals, such as silver and gold. However, upon any object, and especially one that is of irregular shape, the deposit is never of uniform thickness, as there is a tendency for the metal to accumulate upon edges or points or upon parts nearest to the anode. In general, for protective purposes or for durability, the plating on an object is as good as its thinnest part. In some cases, however, as on spoons, it is desirable to have some part, *e.g.*, the outside of the bowl, most heavily plated. It is obvious that no stripping method dependent upon determining the total weight of the deposited metal is any true measure of the distribution of the plating. It may be very useful in detecting very lightly plated work or in comparing products plated under nearly similar conditions. Methods for determining the weight of deposit by stripping will be described under the various metals. It is not possible to prescribe any definite thickness of metal that will protect the base metal. If it were possible to make the initial coating impervious, it would not be necessary to have so thick a coating of those metals such as nickel, which themselves resist corrosion, as of those such as zinc, which are readily attacked or dissolved. The average thickness of a satisfactory commercial nickel coating on brass articles is rarely over 0.0002 in. (0.005 mm.) and is usually less than 0.0001 in. (0.0025 mm.). On iron and steel however, where protection against corrosion is important, the coating of nickel, or of nickel plus copper, is usually about 0.001 in. (0.025 mm.). Zinc coatings required to furnish con-

siderable protection against corrosion are almost always at least 0.0005 in. (0.0125 mm.) and frequently over 0.001 in. (0.025 mm.) in thickness. Cadmium coatings are usually much thinner, *e.g.* about 0.0002 in. (0.005 mm.). Silver deposits on high grade tableware, *e.g.* on that with 6 troy ounces of silver per gross of teaspoons, have an average thickness of about 0.0008 in. (0.020 mm), with the deposit on the wearing part of the bowl about 50 per cent heavier. (This is usually applied by a secondary plating operation.) Chromium coatings when applied primarily for tarnish resistance are only 0.00001 to 0.00005 in. (0.00025 to 0.00125 mm.) thick, but to resist abrasion they may be from 0.0002 to 0.005 in. (0.005 to 0.125 mm.) thick. Gold coatings often yield satisfactory service when they are less than 0.00005 in. (0.00125 mm.) thick.

(b) **Distribution.**—Certain stripping methods have been devised which depend upon a relatively slow but uniform action of a reagent which will not only dissolve the coating but will also give an indication when the base metal is exposed. The most common of such methods is the so-called Preece test for zinc coatings. In this method the zinc-coated article is subjected at about 18°C (64°F.) to the action of a neutral solution of copper sulphate (sp. gr. = 1.186 at 18°C., or 64°F.) for successive periods of 1 min. each until an adherent deposit of copper which will withstand rubbing is produced on some part of the surface. This is considered as evidence that the iron is exposed at that point. According to the number of immersions required, the article is said to withstand two, three, or more "dips." This method has been very extensively used, and has yielded fairly satisfactory results upon zinc coatings produced under similar conditions, *e.g.*, by hot dipping. It is very difficult, however, to coordinate the results obtained with objects coated with zinc by different processes, such as hot dipping, sherardizing, and electroplating. Its use in specification and testing has therefore decreased in recent years, though it is still employed as a convenient field inspection test.

A few years ago C. J. Wernlund[1] described a new dip test for zinc coated articles. This method employs a solution prepared by adding 33 c.c. of glacial acetic acid (CH_3COOH) to 300 c.c. of water, cooling to nearly 0°C. (32°F.) and adding slowly 10 g. of

[1] *Metal Ind.*, vol. 23, p. 13, 1923.

sodium peroxide (Na_2O_2). The solution when diluted to 1 l., contains about 20 g./l. of free acetic acid, and 4 g./l. of hydrogen peroxide (H_2O_2) which is produced by the action of part of the acetic acid on the sodium peroxide. This solution is heated to 95°C. (nearly boiling) and the zinc coated specimens are immersed in it. The time required for the first appearance of rust spots is then noted. This test when properly calibrated indicates the minimum thickness of zinc on the sample tested. So far as known this method has not come into extensive use. One objection to it is that the solution is somewhat unstable, and must therefore be prepared at frequent intervals.

Treatment with nitric acid has been recommended by R. E. Maeder[1] for estimating from the time required for penetration, the local thickness of copper on steel. Similar treatment with hydrochloric acid has been suggested for testing the thickness of chromium deposits. A solution containing hydrochloric acid and antimony chloride has been used for testing both zinc and cadmium coatings. The time used for stripping silver with nitric and sulphuric acid (p. 360) has been used to explore the thickness of silver deposits. At best, all such methods are subject to errors caused by the influence of surface conditions and the structure and purity of the deposit upon the rate of action of the reagent upon the metal coating. They are therefore useful only in a given plant and under exactly comparable conditions. A thorough study of various reagents might lead to the development of solutions which will dissolve such coatings at a uniform and reasonably rapid rate and will indicate when the base metal is exposed.

(c) **Permeability.**—Especially in the case of coatings of metals which do not exert any intrinsic protective action, as *e.g.*, nickel, chromium, lead, or copper upon iron, the value of the deposit depends largely upon its freedom from pin holes or porosity. For detecting such flaws some modification of the "ferroxyl" test may prove very useful. This test depends upon the fact that if coated iron is treated with a reagent containing ferricyanide, a blue color is produced if the iron is exposed and if it dissolves. For iron or steel coated with nickel, chromium, copper, or lead it is only necessary to treat the surface with a solution containing, *e.g.*, about 10 g./l. (1.34 oz./gal. of sodium chloride, 1 g./l. 0.13

[1] *Monthly Rev., Am. Electroplaters Soc.*, vol. 9, no.11, p. 5, 1922.

oz./gal.) of potassium or sodium ferricyanide and 10 g./l. (1.34 oz./gal.) of agar. If iron is exposed at any point, a blue spot will be produced there, usually within a minute or so. In some cases a solution containing ferricyanide and a gum is sprayed on the nickel plated surfaces.

In a recent ingenious modification of this test,[1] strips of white paper are sprayed with the reagent and allowed to dry. Before use they are moistened with water and pressed against the surface to be tested. Blue spots appear on the paper wherever iron is exposed, and thus produce a permanent record of that test. If the steel has been plated with copper and then nickel, a red spot appears on the paper wherever copper is exposed. The ferricyanide test may therefore also be used to detect porosity of nickel coatings on brass, by the appearance of red spots. This test cannot, however, be applied to zinc-coated steel, because in such a combination the zinc will corrode before the steel, and will produce a white precipitate of zinc ferrocyanide which will mask any subsequent action upon the iron.

(d) **Adhesion.**—To be of any permanent value, a plated coating must adhere closely to the base metal. It seems most reasonable that the adhesion of a metal to the metal upon which it is deposited depends primarily upon an intimate contact of the two, *i.e.*, the absence of any film of grease, oxide, gas, or other foreign material. This theory is well illustrated by the adherence of two blocks of metal which have been polished to plane surfaces by "lapping," *i.e.*, by rubbing over each other. Gage blocks so prepared will adhere to each other with a force very much greater than the atmospheric pressure, showing that intimate atomic or molecular forces are involved. It is entirely possible, however, that in certain cases there may be a slight tendency toward the formation of an alloy between the deposit and the base metal, leading to an increased adhesion. Thus it has been observed[2] that when zinc is plated with copper or brass, and is subsequently exposed to somewhat elevated temperatures, there is a tendency for the copper (or the brass) to be absorbed by the zinc. It is then not improbable that such an alloying action may occur even at ordinary temperatures, at the immediate surface of contact between the two metals. In those cases in which the crystals of the electrodeposit rep-

[1] Pitschner, K., *Proc. A.S.T.M.*, vol. 27, part II, p. 304, 1927.

[2] Traub, W. G., *Trans. Am. Electrochem. Soc.*, vol. 42, p. 55, 1922.

resent a continuation of the crystals of the base metal,[1] we must have almost perfect adhesion.

The recent applications of chromium over nickel deposits have emphasized the need for more adherent nickel to prevent it from peeling during the chromium plating process. Whatever is the ultimate cause of the adhesion of a plated metal, it is certain that for practical purposes it is most largely dependent upon thoroughness of preparation of the surface to be plated. It is necessary not only to remove all the grease or foreign material originally present, but also to rinse thoroughly to remove all alkali or soap left from the cleaning solution. In many cases an acid dip, *e.g.* in dilute hydrochloric acid is beneficial, especially before introducing the articles into an acid plating bath such as an acid copper solution. In some cases brass or copper is dipped into a nickel solution with a low pH, for example below 5.0, and then without rinsing is placed in the nickel plating bath.

In addition, it appears probable that best adhesion will be secured when the deposited metal is (1) as nearly free from internal strains as possible, and (2) free from occluded oxides, basic salts, or gases. With nickel these conditions are best realized by using a high content of nickel and of chloride in the bath, a moderately high pH, a high temperature, and a low current density.

It is not a simple matter to determine or specify the degree of adherence of one metal to another, especially in the case of commercial articles of various shapes. In experimental work, comparative tests may be made by depositing upon sheet metal, which is subsequently subjected to bending or other deforming tests. Such a method is, however, of no value for inspection purposes, except for similar material. C. F. Burgess[2] employed for an adhesion test of zinc-coated steel a method in which a piece of metal was soldered to the coated metal, and the force necessary to detach the coating was then measured. This test is, however, of doubtful value since it rests upon the assumption that the adhesion will not be affected by the elevated temperatures employed in soldering. Recently adhesive tape has been applied to plated coatings and then pulled off to see whether the coating detaches. The results are sometimes of qualitative value.

[1] Blum, W. and Rawdon, H. S., *Trans Am. Electrochem Soc.*, vol. 44, p. 305, 1923.

[2] *Electrochem. and Met. Eng.*, vol. 3, p. 17, 1907.

There is a great need for the development of a simple test which can be used to determine the adhesion of plated coatings on finished articles and which will not damage the articles if they are satisfactory.

(e) **Hardness.**—The applications of chromium plating for wear resistance have called attention to the measurement of hardness. At best it is difficult to define just what is meant by the hardness of metals and to measure it in terms that indicate the value of any given purpose. It is still more difficult to make reliable measurements of the hardness of thin plated coatings, as the results are likely to be influenced by the underlying base metal.

The methods that have been most generally used for measuring hardness of metals involve resistance to deformation. The Brinell hardness is measured by determining the width of the depression produced by a steel ball when pressed against the surface of the metal with a definite load. The Rockwell tester is similar in principle, except that the depth of penetration is measured instead of the width of the depression. The scleroscope method measures the distance to which a steel ball rebounds when allowed to drop onto the surface from a definite height. None of these methods is applicable to thin plated coatings, because the results are affected by the properties of the base metal, unless the coating is relatively thick.

D. J. Macnaughton[1] and A. W. Hothersall[2] have made extensive measurements on the Brinell hardness of electrodeposits of nickel and other metals, with a thickness of 0.25 mm. (0.01 in.). Such deposits are over ten times as thick as most commercial plated coatings. The results are therefore chiefly of direct interest in connection with electroforming, and the building up of worn out parts. They have, however, an important bearing on the relation of the hardness to the microstructure of the deposits, and on the effects of solution composition and operating conditions upon the structure and hardness.

"Scratch hardness" measurements have been extensively applied for determining the resistance of a metal to abrasion. In this method a diamond or sapphire point with a small load attached, is drawn across the surface, producing a

[1] Macnaughton, D. J., *J. Iron and Steel Inst.*, vol. 109, p. 409, 1924.

[2] Macnaughton, D. J. and Hothersall, A. W., *Trans. Far. Soc.*, vol. 24, p. 387, 1928.

scratch which is wider in a soft than in a hard material. The average width of this scratch is then measured with a microscope and suitable scale. Recently this method has been applied to deposits of chromium.[1] Results were obtained which showed an appreciable variation in the hardness of the chromium with conditions of deposition. The hardest deposits were produced at the highest current densities (for a given temperature). It is difficult however for different observers to obtain consistent results by this method, especially upon very hard metals such as chromium. This is because the scratch is very fine and its boundaries are not always clearly marked. Until the method is defined more precisely, the results must be considered as merely an indication of relative hardness, rather than a quantitative measure of it.

Other methods of testing hardness or wear resistance that have been suggested, include resistance to abrasion against another metal surface, as in the Amsler machine; and resistance to abrasion by particles of sand forced against the surface in a stream, or pressed against it by a roller. None of these methods has been sufficiently standardized to permit the estimation of their value for plated coatings.

Even more important than the direct measurement of hardness, is the relation of the results to those obtained in actual service. At present it is apparent that it is not possible to predict the wear resistance from hardness measurements except in a general way. Thus there is no doubt that nickel electrotypes last longer than copper, and chromium plated electrotypes last still longer. Similarly gages plated with chromium last longer than do any unplated gages.[2] But small differences in hardness of the nickel or of the chromium such as may be caused by differences in conditions of deposition, are difficult to measure either in the laboratory or in service. Macnaughton and Hothersall (p. 134) obtained much harder deposits of nickel from solutions containing ammonium sulphate than from those containing boric acid. In general they found that, as pointed out on p. 86, the finest grained deposits are the hardest. In most cases an increase in hardness was accompanied by an increased cathode polarization.

[1] Grant, L. E. and Grant, L. F., *Trans. Am. Electrochem., Soc.*, vol. 53, p. 509, 1928.

[2] French, H. J. and Herschman, H. K., *Trans. A.S.S.T.*, vol. 10, p. 683, 1926 and vol. 12, p. 921, 1927.

3. ACCELERATED CORROSION TESTS

In view of the difficulty of defining or measuring the specific properties which determine the value of an electrodeposited article, some form of "service" test may prove useful. If the function of the coating is to furnish resistance to corrosion, an "exposure" test is naturally suggested. The ideal corrosion test would involve exposure to the actual conditions to be met. Unfortunately, however, weather conditions are hard to define or standardize and, moreover, such a test would require a longer period than would be practicable for inspection purposes. Various forms of accelerated corrosion tests have therefore been proposed, some of which have proved useful. It should be recognized that such tests are at best only of approximate and relative value, and useful chiefly for comparing similar samples. It is not possible to interpret the results in terms of "ordinary exposure," for the simple reason that there is no such thing as "ordinary exposure."

Salt Spray Test.—The most commonly used accelerated test is the "salt spray test," which has been used for a number of years and is described in detail in Circular 80 of the Bureau of Standards. In this test the articles are subjected to a fine spray of a 20 per cent solution of sodium chloride and are examined at intervals to determine when corrosion of the base metal occurs. This method is especially useful for testing zinc-coated steel, and during the war it served as the basis of specification for many military supplies. For mild outdoor exposure, resistance to the salt spray for 48 hr. is probably sufficient; for severe exposure 72 hr. should be specified, and for marine exposure at least 96 hr. As previously explained, the average thickness is no necessary criterion of the value of the coating, and hence it is difficult to coordinate the thickness and the resistance to the salt spray test. Simply as a rough guide, however, it may be assumed that if fairly uniformly distributed and of good quality, a zinc coating with a thickness of 0.0005 in. (0.125 mm.) will withstand at least 2 days' exposure to the salt spray, and of 0.001 in. (0.025 mm.) at least 4 days. At best the salt spray test is not quantitative, as the results depend to some extent upon such factors as the temperature, the volume and velocity of air and the size of the sprayed droplets.

The salt spray test when applied to nickel-coated steel serves only to detect permeability, and is not a measure of the thick-

ness. The nickel is not itself readily attacked by sodium chloride and, on the other hand, any large flaws or pores will cause iron rust to appear in a few hours, while rust from fine pores may not appear for a much longer period. The time required for the first appearance of rust on nickel plated steel in the salt spray test is no direct evidence of the protective value of the coating. The number and size of the pores, which can usually be determined more quickly by the ferricyanide test (p. 131) furnishes a better indication of the quality of the coating. E. M. Baker[1] recognized this limitation of the salt spray test, and proposed a numerical scale of rating, dependent upon the time required to produce different degrees of rust. This system is useful in a given plant, but it is hard to standardize it for use by different observers or on different products.

The intermittent immersion test,[2] in which the articles are exposed in cycles to the air and to a solution such as of sodium chloride or of ammonium chloride, gives results similar to those of a spray, but in a shorter time.

In some plants a "humidity test," in which the articles are subjected to 98 per cent humidity at 100°F., is used for testing articles that do not require resistance to more severe conditions.

[1] *Jour. Soc. Automotive Eng.*, vol. 15, p. 127, 1924.

[2] Farnsworth, F. F. and Hocker, C. D., *Trans. Am. Electrochem. Soc.* vol. 45, p. 281, 1924.

CHAPTER IX

PREPARATION FOR ELECTROPLATING

The production of an impervious adherent metal coating depends primarily upon securing a thoroughly clean surface upon the metal to be plated. The two kinds of foreign materials likely to be adherent upon metal surfaces are: (1) oxides (or similar metallic compounds) which constitute rust, scale or tarnish, and (2) grease or oil (or other organic substances). In addition, there may be, especially upon greasy surfaces, almost any material commonly designated as "dirt," which is frequently defined as "matter out of place." In general, however, if the grease and oxides are removed, the other materials will also be eliminated. Oxides are usually removed by mechanical abrasion, or by "pickling," *i.e.*, solution in acids. In the latter method uniform action of the acid is impossible unless the surface is practically free from grease, which must therefore be first removed.

1. REMOVAL OF GREASE

(a) **Definition.**—The term "grease" may be used in a broad sense to include any oily substances. These may have been applied to the metals intentionally, *e.g.*, as "slushing oils" for protection against corrosion during storage, or as "cutting compounds" used during the machining operation, or as constituents of the polishing or buffing "compounds" used in finishing or "coloring" the metal surfaces. Grease may also come from accidental contamination, as, *e.g.*, from oil or perspiration upon the hands.

Whatever the source of these oily substances, they may be divided into two classes, those which are "saponifiable," and those which are not. The best example of a saponifiable grease is an animal or vegetable fat. All such fats contain compounds of some "fatty acid" and an "alcohol." Thus a hard fat, such as stearin (one of the principal constituents of tallow), is a compound of stearic acid and glycerin (which latter substance

belongs to a certain class of alcohols). In other words, a fat is an organic salt, formed by the combination of an organic (fatty) acid, and an organic base or alcohol. When we state that such a compound is "saponifiable" we mean simply that it is capable of being converted into a soap by the action of an alkali. In such a reaction the metal of the alkali replaces and liberates the glycerin of the fat, forming a metallic salt of the fatty acid, *i.e.*, a soap. This reaction may be represented as follows:

Glycerin stearate + Sodium hydroxide = Sodium stearate + Glycerin

(Stearin) (Soap)

Similar reactions occur with other common fats, such as those derived from oleic and palmitic acids, which fats are present in many greases and oils. One marked distinction between a fat and the soap derived from it by the action of a strong alkali (such as sodium or potassium hydroxide) is that the soaps are soluble in water, while the fats are practically insoluble. When saponified, therefore, the oil or grease passes into solution, and is thus removed from the surface to be cleaned.

Unlike the animal and vegetable fats and oils, mineral oils are usually unsaponifiable. Such oils generally consist of hydrocarbons, *i.e.*, compounds of carbon and hydrogen, which are practically unaffected chemically by alkalis. According to their chemical composition, hydrocarbons range in consistency from very light liquids, such as gasoline, to lubricating oils, vaseline, and finally to solids such as paraffin, all of which are very similar in certain chemical properties.

(b) **Use of Organic Solvents.**—All classes of grease can be removed from metals by means of suitable organic solvents, such as gasoline, benzene (benzol), xylene (xylol), carbon tetrachloride, etc. This process depends simply upon the physical solvent action of these compounds and not upon any chemical reaction. In effect, the grease or oil is diluted by the solvent. If after such a liquid is used for the removal of grease, it is distilled, the solvent may be recovered practically pure, and the grease or oil is left in the still. This method of recovering the solvent for further use is frequently employed commercially. Owing to the inflammability of gasoline and benzene, their use for the removal of grease is attended with grave fire hazards. These may be reduced by the use of automatic extinguishing equipment, containing for example fusible plugs. The vapors, especially those

of benzene (benzol), are also injurious to the health. If conditions appear to warrant the use of an organic solvent, *e.g.*, if the objects are heavily coated with oil or grease, a non-inflammable liquid, such as carbon tetrachloride, or a mixture of carbon tetrachloride and gasoline, should be employed. In any case this method is not adapted for complete cleansing, as the liquid when it evaporates from the surfaces will usually leave at least a thin film of grease, the amount of which increases with continued use of the solvent.

(c) **Emulsification.**—Formerly strong, hot alkali solutions such as caustic soda or potash, were almost exclusively used for removing grease from metals, probably upon the assumption that the grease would be thereby saponified and removed as a soluble soap. According to the present accepted theories, such cleansing action is due not so much to saponification as to "emulsification." By emulsification is meant the suspension of one liquid in another in the form of very minute drops or globules. A familiar example of an emulsion is milk, in which the fat globules are suspended in a nearly neutral solution (containing in addition to the alkaline salts, dissolved sugar, and a colloidal suspension of solid casein). An emulsion of two liquids is in effect a colloidal solution (page 102) in which the suspended particles are liquid instead of solid as in ordinary colloidal solutions.

The ability of one liquid to form an emulsion with another liquid is determined largely by its "surface tension," *i.e.*, the strength of the film upon a surface of the liquid. This in turn is markedly affected by the hydrogen ion concentration (acidity or alkalinity) of a solution, and by the presence of certain substances such as soaps. The action of the soap solution is probably due largely to the fact that in it much of the soap is present in colloidal suspension. Other colloids, such as gums, may be used to promote the formation of emulsions.

Recognition of the fact that even slightly alkaline solutions containing colloids such as soap, have the power to cause emulsification of fat and grease, and thereby to remove them from metallic surfaces, has led within recent years to the substitution of more mildly alkaline solutions than those formerly employed. If all that is required is to obtain a slightly alkaline solution, it might at first appear desirable to use simply a very dilute solution of caustic soda or potash. If, however, this were done, the solution would readily become weakened by dilution, by absorp-

tion of carbon dioxide from the air, by neutralization from acid fumes or spray, or by saponification of any fats present on the metal. It is therefore advisable to employ a solution of a salt which is readily hydrolyzed with the formation of free alkali, or hydroxyl ions (page 32). One of the simplest and most commonly used substances for this purpose is sodium carbonate (Na_2CO_3), usually purchased in the form of "soda ash." Owing to "hydrolysis" a solution of sodium carbonate contains an appreciable amount of sodium hydroxide, and an equivalent amount of carbonic acid. As, however, the sodium hydroxide is a stronger base (*i.e.*, is more completely dissociated) than the carbonic acid is an acid, the solution has an alkaline reaction, as can be readily shown by common indicators such as litmus. If by any means this slight alkalinity is neutralized, the remaining sodium carbonate hydrolyzes to form more free alkali, thus serving in effect as a reservoir of alkalinity.

Practically all commercial metal cleaners contain a large proportion of sodium carbonate. Other substances which may serve to furnish by hydrolysis a constant slight alkalinity, are trisodium phosphate (Na_3PO_4), sodium silicate (Na_2SiO_3), sodium aluminate ($NaAlO_2$), sodium cyanide (NaCN), and sodium borate (borax, $Na_2B_4O_7$). The sodium silicate and sodium aluminate also give rise through hydrolysis to colloids, which may assist in emulsification.

In addition to these alkaline compounds, most cleaning mixtures contain at least a small amount of free alkali, usually sodium hydroxide. This serves to act upon any saponifiable fat, whereby it not only cleans the metal, but also produces in the solution a soap, which then assists in the emulsification of unsaponifiable grease. In many cases, especially if there is little or no saponifiable fat present on the metal, soap is added to the solution; or substances such as rosin are added, which when heated with the alkaline solution are converted into soaps. The principal objection to the use of rosin soaps in cleaners is that they are not readily soluble in cold water, and consequently in the rinsing of the articles a film of rosin soap may be left upon the article which would prevent subsequent adherence of the deposit, and would therefore be as objectionable as the original grease. Very concentrated caustic soda solutions are objectionable because in them soaps are nearly insoluble and may be precipitated on the metal.

In a valuable study of alkaline solutions by E. M. Baker and R. Schneidewind,[1] the cleaning efficiency was measured by the ability to form emulsions with a heavy mineral oil. From these data, it was concluded that sodium hydroxide (NaOH) and trisodium phosphate (Na_3PO_4) are both very effective cleaners, but the latter is better because it has less tendency to stain the metal, is more easily rinsed and forms less stable emulsions. Soaps are very effective cleaners, but are difficult to rinse. Soaps made of unsaturated acids (such as those in linseed oil and fish oil), and those made with potash instead of soda, rinse more freely. Sodium silicate (water glass) is a good substitute for soap. There is still considerable doubt as to the relation of the pH of the cleaning solutions to their effectiveness. This subject deserves more study.

Cleaners should be used as hot as possible. Oils which separate out on the surface of a used cleaner may be skimmed off in the morning before the cleaner is heated, and thus increase its efficiency.

(d) **Effect of Solid Particles in Cleaning Solutions.**—Within recent years several proprietary cleaners have been prepared which contain appreciable amounts of insoluble materials, such as finely divided silica or silicates, alumina, etc. These were at first viewed by many as "fillers," added solely for the purpose of adulteration. There is good reason to believe, however, that in some cases at least they serve a useful function, and that they do materially assist in the removal of grease. The simplest explanation of their action would be that it is due to a mechanical scouring of the surface, *i.e.*, the solid particles may by agitation be driven against the surface in such a way as to remove the grease. This behavior is analogous to the action of a sand blast driven by a liquid instead of by air.

It is also possible that the removal of the grease is due to the large total surface of the very fine particles, and the adsorption upon this surface of the grease or oil. This effect is involved in the explanation given by W. D. Bancroft[2] that an emulsifying effect of solid particles is due to the fact that they readily pass into the "interface" between the oil and water, and thereby render the emulsion more stable. In other words, each particle

[1] *Trans. Am. Electrochem. Soc.*, vol. 45, p. 237, 1924.

[2] "Applied Colloid Chemistry," 2nd edition, p. 264, McGraw-Hill Book Company, Inc., 1927.

of oil, as it passes into the emulsion, becomes coated with a layer of the fine powder, and hence is prevented from coalescing with other drops of oil.

The fact observed by O. P. Watts,[1] that the finest powders are most effective in aiding the cleansing, supports the latter theory. He found that almost any finely divided solids suspended in hot alkaline solutions, or even in water, have a marked cleansing action upon greasy metal surfaces.

According to the results of Hofmann, quoted by Bancroft, almost all of the powders found efficacious by Watts pass into the interface when treated with water and paraffin oil. Detailed study of this subject may lead to the development of greatly improved cleaning solutions. In any case it is obvious that such solids are effective only when they are fine enough to to be kept readily in suspension.

One possible objection to the presence of suspended particles in solutions used in electrolytic cleaning, is that they may be carried to the cathode and adhere to it, and cause pitting of the subsequent deposits (p 244).

(e) **Electrolytic Cleaning.**—Somewhat analogous to the action of finely divided solids is that of finely divided gases, such as are produced upon the cathode in the process known as electrolytic cleaning. In this process almost any of the alkaline solutions ordinarily used may be employed, provided that there is a fairly high content of alkali or alkaline salts, such as sodium phosphate or carbonate, to cause good conductivity. The objects to be cleaned are hung on the cathode bar, and an iron anode is used, or more frequently the iron tank is made the anode. Separate anodes are preferable as they can be removed and cleaned at intervals. An e.m.f. of from 6 to 12 volts is applied, *i.e.*, sufficient to produce a current density of at least 10 amp./sq. ft. (1 amp./dm.^{2}), which causes vigorous evolution of gas (hydrogen) upon the cathodes. The increased cleansing action no doubt depends in part upon the formation at the cathode of free alkali, but is due also to the mechanical action of the hydrogen, which is evolved on the metal surface and therefore tends to lift the oil film and to assist in its emulsification. In addition, the gas evolution causes agitation of the solution and hence constantly brings fresh portions of the constituents to the cathode surface.

[1] *Monthly Rev. Am. Electroplaters' Soc.*, vol. 8, p. 4, 1921.

When brass and surfaces containing solder are cleaned, there is a tendency for zinc, tin, and lead to dissolve in the alkaline solutions. If this occurs in a solution used for electrolytic cleaning, a small amount of these metals may be redeposited upon the surface in a film which will prevent subsequent adherence of a nickel deposit. Where such conditions exist, it is frequently found desirable to connect with the cleaning tank a double throw switch, so that after the work is cleaned for, *e.g.*, 3 to 5 min. as cathode, it may be made the anode for 10 or 15 seconds, during which latter period any film of zinc, tin, or lead is redissolved. By this means it is frequently found that more adherent deposits are secured than by the ordinary method. Instead of carrying out the direct and reverse current cleaning in one tank, it is preferable to use two tanks, in the first of which the articles are hung as cathodes, and in the second as anodes.

(f) **Typical Cleaning Solutions.**—As above indicated, cleaning mixtures or solutions are likely to contain at least four types of substances: (1) free alkali; (2) salts of weak acids, which give rise through hydrolysis to alkali, *i.e.*, to hydroxyl ions; (3) soaps, or materials which will react with the alkali to form soaps; and (4) inert suspended matter. As there are a large number of possibly useful substances in each of these classes—with the exception of (1)—it is obvious that an almost innumerable variety of cleaning "compounds" may be prepared. Moreover, the amounts and kinds of grease likely to be present upon metal articles to be plated are quite variable in different plants or upon different classes of work. More consideration should be given to the kinds of oil and grease used in manufacturing and polishing operations, with special reference to the ease with which they can be subsequently removed. Frequently this will lead to changes which, without extra cost, will reduce greatly the time and expense of cleaning. In general, those greases should be used of which the saponifiable parts form readily soluble soaps.

It is not surprising that many electroplaters and others who have metal surfaces to clean find that some particular mixture, used under certain conditions, meets their requirements satisfactorily, and consider it impossible to use any other. It is fairly safe to say that in most cases the difference between a good and a poor cleaner for a given class of work is the time required to produce a clean surface; in other words, almost any

hot alkaline solution will in time remove all grease from a metal surface.

Under these conditions the use of "proprietary" or prepared cleaners is certain to continue for a long time. When such products meet specific needs their use may be justified, provided their composition is known to the operator, so that he can use them intelligently, and, if need be, adapt them to unusual conditions. If the formulas of all such products were marked upon the containers, the purchaser could assure himself as to whether he was paying a reasonable price for the convenience of having a uniform mixture prepared for him. Too often the assumption is made that a high-priced cleaner must necessarily be superior to one of moderate price which may, in fact, have a practically identical composition.

A typical simple cleaning solution, which may at least be used as a basis to which other materials may be added, may be prepared from 8 oz./gal. (60 g./l.) of sodium carbonate (soda ash. Na_2CO_3) (or the equivalent—22 oz./gal. or 165 g./l.—of the crystals, $Na_2CO_3.10H_2O$), and 2 oz./gal. (15 g./l.) of sodium hydroxide (NaOH). The same result can be obtained by dissolving 10 oz./gal. (75 g./l.) of 20 per cent causticized soda ash. Trisodium phosphate (Na_3PO_4) may be used to replace all or part of the sodium carbonate. Sodium cyanide (NaCN), in amounts of about 1 oz./gal. (7.5 g./l.), will often be found advantageous in removing or preventing stains, especially in electrolytic cleaners for brass, etc. In view of the great variety of cleaning solutions used commercially, there would be little advantage in attempting to specify formulas for specific classes of work. Especially where the occasional services of a chemist are available, it should be readily possible to develop and maintain solutions to meet any given requirements.

Due consideration should also be given to the possible chemical action of the cleaning solution upon the metal to be plated. Aluminum, zinc, tin, and lead are all readily attacked by caustic alkali, which should not be present in appreciable amounts for cleaning such metals or alloys containing them, such as die castings. For such cases it is better to use solutions containing only carbonates, or, better still, containing some sodium bicarbonate ($NaHCO_3$). In some cases carbonate and bicarbonate are crystallized together in a form known as sodium "sesquicarbonate" ($Na_2CO_3.NaHCO_3.2H_2O$). For cleaning metals

easily attacked by alkalis, very hot concentrated solutions of soap (e.g., a good quality of soap chips or fish oil soaps) are often used, especially when only buffing or polishing grease is to be removed. Sometimes a small amount of sodium carbonate, ammonia, or borax is added to the soap solution.

For mass production the use of a double cleaning system is generally useful. Thus the articles may be first cleaned in a strong hot soap solution, rinsed in hot water and then passed through an electrolytic cleaner. In any case it is desirable to heat the cleaning solutions up to nearly 212°F. (100°C.), which can be readily accomplished by means of low-pressure steam coils. The use of live steam is objectionable as it dilutes the solutions. The advantage of heated solutions depends upon (1) the increased hydrolysis and consequently greater alkalinity of the hot solutions, (2) the increased rate of saponification of any fats, (3) the greater solubility of any soap that may be formed by saponification, and (4) the circulation produced by the convection currents during heating. This circulation is best accomplished by having the steam coil toward the front (working side) of the tank, somewhat above the bottom, so that the ascending current of solution tends to keep the surface clean where the work is suspended, and to carry the scum, etc., toward the back where it may be removed.

2. REMOVAL OF OXIDES

The removal of oxides, etc., which form the scale, rust, or tarnish on metals, is frequently accomplished by pickling with acid. The choice of acid to be used is determined by the nature of the metal and of the scale to be removed from it. In general, for iron and steel, sulphuric or hydrochloric acid (and occasionally hydrofluoric acid) is employed, while for brass, sulphuric and nitric acids are used.

(a) **Treatment of Brass.**—The electroplater is sometimes called upon to clean brass carrying oxide scale produced during brazing or hard soldering. To do so the brass should be pickled in sulphuric acid, containing 60 g./l. (8 oz./gal.) of H_2SO_4.

After such pickling, it is customary to put the brass through a preliminary "scaling dip" or "black boil." This is a strong pickle, containing about 50 per cent more nitric acid, slightly more hydrochloric acid, and about 25 per cent less sulphuric acid than the regular bright dip (see below). This is generally

made by adding nitric and hydrochloric acids (and if necessary sulphuric acid) to a "spent" bright dip. Too much nitric acid will roughen the brass. The brass comes out of such a dip dull and often covered with a thin "smut." It readily acquires a bright color, however, by subsequent immersion in a bright dip. If the brass is fairly clean, the so-called "bright dipping" is sufficient to produce a clean surface for plating. In this process a mixture of nitric and sulphuric acids containing a small amount of hydrochloric acid is employed.

The following are typical formulas for preparing dips. The actual composition varies for different kinds of brass or for different finishes. Moreover, the composition changes rapidly during use, owing to the consumption of acid and the accumulation of zinc and copper salts. Small additions of hydrochloric acid, *e.g.*, 1 fluid oz. to 40 gallons (0.025 fl. oz./gal.), are made at regular intervals to obtain the maximum brightness. The dips are kept in stoneware jars, surrounded by running water, in order to prevent the temperature from exceeding 40°C. (94°F.).

A. K. Graham[1] in one of the few published articles on bright dips, has shown the effects of each of the constituents in the dip upon the rate of attack of the copper and zinc in the brass. He has recommended the following formulas for bulk dipping. This bright dip is more dilute than that used for individual pieces. This is because in bulk dipping it is more difficult to control the time of dipping and to rinse the articles quickly.

FORMULAS FOR DIPPINGS[1]
(Derived from A. K. Graham)

	Sp. gr.	°Bé.	Scaling dip			Bright dip		
			g./l.	cc./l.	Fl. oz./gal.	g./l.	cc./l.	Fl. oz./gal.
H_2SO_4.....	1.84	66	700	380	48.0	800	435	54.00
HNO_3.....	1.38	40	100	72	9.0	100	72	9.00
HCl.....	1.17	20	5	4	0.5	25	2	0.25
H_2O.....	....	..	544	544	68.0	491	491	61.00

[1] The volume relations have been computed upon the assumption that the reduction in volume upon mixing is negligible. Actually the volume produced will be about 3 to 5 per cent less than the sum of the volumes of the original separate liquids.

[1] *Trans. Am. Electrochem. Soc.*, vol. 52, p. 289, 1927.

Frequently finely divided carbon, introduced in the form of soot, lampblack, bran, etc., is added to bright dips, forming a "cover" over the surface. In some unexplained way, the presence of this carbon favors uniform attack of the brass, and thus counteracts any tendency to attack the metal in spots. If an excess of hydrochloric acid is in the dip, it causes the brass to have a smoky or clouded color. This effect may be overcome by mixing a small amount of soot with the dip and skimming it off after it has been allowed to come to the surface. These observations indicate strongly that the effects of the carbon are due to selective adsorption of one of the acids or of the products of the reaction. It is well known that finely divided carbon has marked adsorptive properties for various substances.

Analysis of Bright Dips.—An approximate determination of the nitric and sulphuric acid content of a bright dip may be made as follows. The solutions required are:

(1) Two normal sodium hydroxide, which may be standardized against a standard solution of hydrochloric acid (page 47).

(2) Normal nitric acid, standardized against the 2 normal sodium hydroxide.

(3) Molar ferrous sulphate solution, containing 278 g./l. of the crystallized salt ($FeSO_4.7H_2O$) and 450 g./l. (250 c.c.) of sulphuric acid. This is standardized against the normal nitric acid, of which, *e.g.*, 15 c.c. is treated with 10 c.c. of concentrated sulphuric acid and then titrated with the ferrous sulphate solution to the appearance of a faint red color. The exact reactions involved in the formation of this color are not known. The ferrous salt is oxidized to ferric salt by the nitric acid, which is itself reduced to nitric oxide (NO) by such an equation as the following:

$$6FeSO_4 + 2HNO_3 + 3H_2SO_4 = 3Fe_2(SO_4)_3 + 2NO + 4H_2O$$

The nitric oxide combines with the ferrous sulphate, as soon as an excess of the latter is present, to form an unstable addition compound, sometimes written $FeSO_4.NO$, which has a reddish-brown to black color. According to the above equation, one molecule of nitric acid requires three molecules of ferrous sulplate. Therefore, 1 c.c. of *N* HNO_3 will require 3 c.c. of *M* (molar) $FeSO_4$. Instead, therefore, of determining or expressing the normality of the ferrous sulphate in terms either of its metal content or its reducing value, it is most convenient to compute its equivalent of normal nitric acid.

The analysis is conducted as follows: A 5-c.c. sample of the bright dip is diluted with water to 150 c.c., two drops of methyl orange solution added, and the solution is titrated with the 2 *N* NaOH till the color changes from red to yellow. From this titration the total acidity (of $H_2SO_4 + HNO_3$) is computed. (The content of HCl is practically negligible in this analysis.)

To another 5 c.c. portion, 10 c.c. of concentrated sulphuric acid is added, and, after cooling, the mixture is titrated with the ferrous sulphate till a faint red or brownish color is produced. From this titration the content of nitric acid is calculated, and if its normality is deducted from the total acidity, the result is the sulphuric acid content.

Problem.—Suppose that, by the usual standardization, the NaOH solution was found to be 1.97 *N*. If, then, 25 c.c. of the HNO_3 solution required 13.2 c.c. of NaOH, the former must be $\frac{13.2}{25} \times 1.97 = 1.04$ *N*.

If in standardizing, 5 c.c. of this HNO_3 required 13.6 c.c. of $FeSO_4$, each cubic centimeter of the latter is equivalent to $\frac{5}{13.6} \times 1.04 = 0.38$ c.c. of *N* HNO_3 with respect to the above reaction.

If a 5-c.c. sample of the acid dip requires 61 c.c. of the standard NaOH, the total acidity is $\frac{61}{5} \times 1.97 = 24.1$ *N*.

If 5 c.c. of the acid dip required 45.2 c.c. of the ferrous sulphate solution, the nitric acid content must be $\frac{45.2}{5} \times 0.38 = 3.4\ N = 3.4 \times 63 = 214$ g./l. HNO_3.

The sulphuric acid content must be $24.1 - 3.4 = 20.7\ N = 20.7 \times 49 = 1{,}014$ g./l. H_2SO_4.

When chemical analyses are not available, the bright dips can be adjusted by the following simple and approximate method. The specific gravity is taken after the dip has cooled. If this is below 1.34 (37° Bé.), concentrated sulphuric acid is added till the specific gravity is about 1.41 (42° Bé.). After cooling to ordinary temperature, concentrated nitric acid is added until a test strip of brass becomes bright on dipping. Occasionally a little hydrochloric acid is added.

(b) **Pickling of Iron and Steel.**—For the pickling of iron and steel, sulphuric acid is most largely employed, principally because of its cheapness. Hydrochloric (muriatic) acid is in certain respects preferable, as it acts more quickly upon iron oxide and does not attack the steel or iron any more rapidly

than does sulphuric acid. Its greater cost is, however, an obstacle to its more general use. The removal of oxides, especially heavy scale, by acid, depends not only upon the actual solution of the oxide, but also its detachment by the bubbles of hydrogen liberated on the surface of the steel. Consequently, some action of the acid on the metal is frequently beneficial in reducing the actual consumption of acid. In general, agitation of the pickling bath reduces the time required for pickling. Intermittent exposure to the acid and to air is also beneficial.

Sulphuric acid pickle usually contains about 10 per cent by weight, or about 100 g./l. of H_2SO_4, *i.e.*, it is approximately 2 *N*. This may be prepared by mixing ½ pt. (about 1 lb.) of commercial acid with 1 gal. of water. This is usually heated (after mixing) to about 50°C. (120°F.) in order to increase the rate of its action upon the oxide. The length of time required will depend upon the thickness and denseness of the rust or scale, and will vary from 10 min. to 1 hr. or more. When hydrochloric acid is used, a solution of about chemically equivalent strength (2 *N*), which contains 73 g./l. of (gaseous) HCl, or about 7 per cent by weight, is usually employed. This requires about 1.25 pt. (1.5 lb.) of commercial hydrochloric acid to 1 gal. of water. As it requires about 1.5 times as much (by weight) of commercial hydrochloric acid as of sulphuric acid to produce chemically equivalent solutions, and as the hydrochloric acid costs more per pound, the use of hydrochloric acid for pickling is even more expensive than would at first appear. Where the amounts used, however, are not very large, its advantages may compensate for this increased cost.

Hydrofluoric acid (HF) is chiefly used for picking iron castings in the surface of which grains of sand may be imbedded, which must be removed prior to finishing. Similarly, steel which has been sand-blasted with too great a pressure may have sand imbedded in the surface, in which case hydrofluoric acid pickling may be advantageous. Silica is readily dissolved by hydrofluoric acid. This acid is also used in a strength of about 2 *N*, *i.e.*, 40 g./l. of HF, or about 4 per cent by weight. Using the 48 to 52 per cent commercial hydrofluoric acid, it will require about ½ pt. (0.7 lb.) of acid for each gallon of water. Frequently a small amount of sulphuric acid is added (in addition to that usually present as an impurity in commercial hydrofluoric acid).

As a substitute for sulphuric acid, especially during the war, sodium acid sulphate ($NaHSO_4$), sold also as "niter cake" and by various trade names, was extensively used. This substance is a by-product in the manufacture of nitric acid from sodium nitrate, and as nitric acid was required in large quantities in the production of explosives, the niter cake was then practically a waste product. Its use in pickling depends upon the fact that only one-half the acidity of the sulphuric acid has been neutralized, and therefore when the substance is dissolved in water the solution contains in effect free sulphuric acid and sodium sulphate. Owing to the presence of the sodium sulphate, however, the sulphuric acid is not dissociated to as great an extent as in a solution of the same sulphuric acid concentration free from sodium sulphate. In consequence, in order to secure the same rate of pickling, it is necessary to heat the acid sulphate baths to higher temperatures than are used with ordinary sulphuric acid pickle.

In recent years various addition agents or "inhibitors" have been used in pickling baths for the purpose of producing more uniform pickling, decreasing the attack on the metal and reducing the amount of spray carried into the air by the evolved hydrogen. Many such materials are proprietary and of unknown composition; others contain common substances such as flour, dextrin, extracts from the sulphite wood pulp process, and pyridine derivatives, obtained from bone oil. Their exact function is not known, but their effects are probably due to the colloids which they generally contain. Such colloids are known to change the overvoltage of hydrogen, and may thus cause exposed steel to be less attacked by the acid. In addition they may change the surface tension of the liquids, and thus cause the hydrogen to be evolved in larger bubbles, which do not carry so much spray into the air. Inhibitors should not, however, be used in electrolytic pickling, as they may produce foam and increase the danger of an explosion from sparks.

(c) **Embrittlement by Pickling.**—One of the most important considerations in the pickling of iron and steel is the effect upon the physical properties, especially the brittleness, of the metal. It is well known that steels, especially tempered spring steels, may be rendered quite brittle by pickling. An investigation of this subject was made by S. C. Langdon and M. A. Grossman.[1]

[1] *Trans. Am. Electrochem. Soc.*, vol. 37, p. 543, 1920.

Their results showed that practically the same degree of brittleness is produced, either in rods or plates, by similar treatments with hydrochloric, hydrofluoric, or sulphuric acids, or with niter cake. It was found, however, that, at most, only slight brittleness was caused by pickling in nitric acid. As in all cases except the latter, hydrogen is evolved at the surface of the steel during pickling, it appears probable that the brittleness is associated with absorption by the metal of hydrogen in some form. This view was confirmed by the fact that this brittleness is largely temporary, *i.e.*, it disappears almost completely when the steel stands at ordinary temperatures for a few days; at elevated temperatures (100° to 150°C., or 212° to 300°F.) for a few hours; or in boiling water for a few minutes. The time required to produce or to remove brittleness also depends upon the composition of the steel. The results indicated that the "permanent" brittleness and also that caused by nitric acid were due largely to roughening of the metal surface.

In this connection reference may be made to the embrittling effect of plating upon steel, especially hardened steel springs, etc. In the investigation above referred to, it was planned to study also this effect of plating, but it was possible to conduct only a few experimeuts. These indicated that the effects due to plating with zinc were similar in sulphate or cyanide solutions, and that the brittleness could be at least partly overcome by subsequent exposure to high temperatures. It is probable that to some extent the embrittlement caused by plating has been overestimated, as such effects are largely temporary. There is need, however, for a careful study of this subject, with special reference to whether brittleness is more pronounced under some conditions. If, as seems probable, the embrittlement is due to absorption of hydrogen by the steel, it is reasonable to expect that those conditions, such as high metal concentration, low current density, and the use of warmed or agitated solutions, all of which tend to produce high metal cathode efficiency, are favorable for prevention of brittleness.

(d) **Mechanical Abrasion.**—Very frequently it is found convenient to remove oxides by mechanical abrasion, *e.g.*, by sandblasting. This method is especially applicable when there is no large amount of grease (which would readily contaminate the sand), and where there is a considerable amount of scale, the removal of which by pickling would require a long period or an

excessive consumption of acid. It is also used where a matte finish is desired. In sand-blasting apparatus the cleaning depends solely upon the effect of a stream of sand or of steel shot.

In any case the effects are purely mechanical, and therefore we would at first assume that no change would be produced in the physical properties of the steel. Actually, however, the process of blasting (with either sand or steel shot) may cause a marked effect upon the properties, especially of thin sheets or small rods. Such effects are probably due to a "cold working" of the surface, which causes hardening and in some cases brittleness. Part of the latter effect is due to the roughening of the surface and possibly to imbedding of sand or steel particles in the surface. Such effects are permanent and may therefore be more detrimental than the effects of pickling, which latter effects may be partly eliminated by appropriate treatment. While, therefore, sand-blasting may be a very efficient means of cleaning metal, it is not safe to assume that it is in all cases preferable to pickling. The fact that it roughens the surface is sometimes an advantage in improving adherence of deposits. It is also probable that such adhesion is promoted by the fact that in sand-blasting there is no opportunity for absorption of gas or liquid by the metal preparatory to plating. If, however, excessive pressure is used in sand-blasting, sand may be imbedded and prevent proper plating unless it is removed by hydrofluoric acid treatment.

"Sand-rolling" is used when it is desired to subsequently polish the surface. By removing burrs and roughness, it greatly reduces the labor required for the final polishing. In sand-rolling, an abrasive such as sand, quartz, silex, pumice, slag, alundum, or emery is mixed with water or oil and the articles are rolled in suitable steel barrels for periods up to several days. Sodium carbonate or hydroxide is often added to the water used in rolling steel, in order to prevent corrosion.

Various other methods of cleaning usually depend upon some mechanical process, such as scrubbing with brushes, using either alkaline solutions alone or together with pumice or other abrasives. Such methods are usually effective but expensive, especially when any large production is involved. The most important economic consideration in cleaning metals commercially is the elimination of hand labor.

Treatment of metal surfaces for the purpose of polishing or of producing any desired finish prior to plating may produce effects similar to those observed in the mechanical cleaning operations. Thus, *e.g.*, in buffing and ball burnishing there is at least a tendency for the metal to "flow," or to undergo cold working which may materially change the structure of the surface film. Such effects are important in view of the great influence which the structure of the base metal exerts upon that of the deposit (page 109). To the extent that by such treatment the surface is rendered more uniform, it may improve the quality as well as the appearance of the deposit.

CHAPTER X

PREPARATION FOR ELECTROFORMING

1. TREATMENT OF METALLIC SURFACES

In order to produce or reproduce an object by electrodeposition, it is necessary to have a mold or form on which to deposit. For accurate reproduction, this mold must be a "negative" of the object to be produced. In certain cases where no great accuracy is required, as in making tubes, etc., it is possible to use as a mold a "positive," which can subsequently be removed by melting or dissolving out the "core."

Whenever a metal mold can be applied in electroforming, it has the great advantage that the surface is conducting and needs no treatment except for insuring the subsequent separation of the deposited metal. Metal molds (or negatives) for the electrolytic reproduction of articles may be made in three ways, *viz.*, by casting, by pressure, and by electrodeposition.

In the first method a low-melting metal or alloy is usually employed, which facilitates not only the original casting, but also the subsequent removal of the metal "core" by melting it out. The most readily fusible alloy is "Wood's metal," which melts at 71°C. (160°F.) and has the following composition:

Composition of Wood's Metal

	Per Cent by Weight
Bismuth	50.0
Lead	25.0
Tin	12.5
Cadmium	12.5

Such an alloy is rather expensive, especially for use on a large scale. A somewhat similar but cheaper alloy with a melting point of about 100°C. (212°F), consists of 25 per cent bismuth, 50 per cent lead, 23 per cent tin, and 2 per cent cadmium.

The manufacture of metal molds for electrodeposition by pressure is practically confined to nearly flat surfaces. The best illustration of this procedure is in lead mold electrotyping

(page 168). In certain cases "deep" lead molding has been accomplished by suitably applied hydraulic pressure.

The use of electrodeposited negatives is customary only when the original or "master" is of metal; or when it is necessary to go through several stages of reproduction. It is the most accurate method of reproducing a metallic surface. Unpublished experiments conducted at the Bureau of Standards have shown that it is possible to reproduce faithfully by the electrodeposition of nickel not only those engraved lines on a steel scale, which are about 0.0005 mm. (0.00002 in.) in width, but also smaller scratches just at the limit of visibility with present microscopic methods. Electrolytic production of negatives is relatively slow and expensive and is therefore used only when accuracy is the prime consideration.

The most important example of the use of electrodeposited negatives is in the phonograph industry. The original wax record is first coated with graphite, upon which copper is deposited to form a "master matrix," which is a negative. From this plate one or more "master records" are made by electrodeposition. The plates are positives, and serve as the forms on which the final or "pressing matrices" or "working masters" are deposited. The latter are sometimes nickel plated, but best results are obtained by making the initial deposit of nickel. A surface of chromium will obviously increase their resistance to abrasion. The fact that satisfactory results can be obtained even after several "generations" of plates have been made is good evidence of the accuracy of reproduction.

In the use of metal forms, the principal difficulty is that of treating the surface so as to permit subsequent separation. The problem resolves itself into the production of a surface which will still be conducting, but which is not "clean," *i.e.*, the deposited metal is not in sufficiently intimate contact with the metal of the mold to cause permanent adherence.

(a) **Mechanical Films.**—The simplest method of securing separation is to apply to the surface a thin layer of some substance which leaves a mechanical film. Grease, or a solution of grease in gasoline, is sometimes used, but it requires very great care to avoid leaving an excess in lines, etc. Graphite is usually very satisfactory, as it can be rubbed on thoroughly either in a dry form or in suspension in water, and the excess removed by a powerful jet of water. When dry graphite is used it is often

advantageous to wash the surface with denatured alcohol in order to prevent air bubbles from sticking in the lines. The amount or thickness of graphite that sticks permanently to a metal surface is so small that it produces no detectable effect on the design.

(b) **Chemical Films.**—A uniformly distributed film can usually be produced by treating the previously cleaned metal surface with some chemical which will react with the metal and produce an insoluble compound. One of the simplest substances for this purpose is a soluble sulphide, such as sodium sulphide (Na_2S), or the yellow "polysulphide" (Na_2S_x). This will react with almost all metals including lead (and its alloys), copper, silver, nickel, and iron to form films of the corresponding sulphides. The chief difficulty in the use of this method is that it is hard to define or control the rate of the action on the surface, and in consequence there is grave danger of insufficient action, which causes sticking, or of excessive action, which may produce premature separation. A typical separating solution for lead or copper contains 7.5 g./l. (1 oz./gal.) of sodium sulphide crystals. Stronger solutions are required to act upon nickel.

Other frequently used compounds are sodium chromate (Na_2CrO_4) and bichromate ($Na_2Cr_2O_7$), or the corresponding potassium salts. These act readily upon lead (page 169) and silver to form insoluble chromates. They are also often used on nickel, which they probably render passive. A dilute solution, containing at most about 4 g./l. (0.5 oz./gal.) of one of the above compounds, is often used.

It is also possible to obtain separation of nickel from a nickel surface by first making the original surface anodic in sodium hydroxide solution. This renders the surface passive, probably by forming an oxide film.

For separating copper forms, *e.g.*, in the phonograph industry, a film of silver iodide may be employed. This is formed by first treating the copper surface with a silver cyanide solution, of which the following is a typical formula:

	Approx. *N*	g./l.	oz./gal.
Silver cyanide	0.3	37.5	5.0
or Silver chloride	0.3	40.0	5.3
Sodium cyanide	1.8	90.0	12.0

This is either poured over the previously cleaned copper surface, or preferably is mixed with an inert substance, such as whiting or calcium carbonate ($CaCO_3$), to form a paste which is rubbed over the copper. A thin film of silver is thus deposited on the copper by replacement. This film is treated with a weak iodine solution, which may be prepared by diluting with water to 1 gal., 1 fluid oz. (or about 8 c.c. to 1 l.) of the pharmaceutical tincture of iodine, which has the following composition:

	g./l.
Iodine	70
Potassium iodide	50
Water	50 (c.c.)
Alcohol to make 1,000 c.c.	

The iodine solution acts upon the silver to form a thin film of silver iodide, upon which copper can then be deposited and subsequently separated.

2. TREATMENT OF NON-METALLIC SURFACES

In order to deposit metal upon any non-conducting surface, it is often necessary to employ two operations, *viz.*, to make the surface impervious to the depositing solutions and to render it conductive. Among the substances which must be rendered impervious are wood (and other forms of cellulose, as in leaves, flowers, etc.) and plaster of paris.

(a) **Making Surfaces Impervious.**—The two simplest methods of excluding the solutions are by treatment with varnishes and with waxes. Shellac and many "spar" varnishes and lacquers of the low viscosity pyroxylin type are practically waterproof. Varnishes containing rubber, which are now being made, may prove very useful. These may be applied to the surface of wood, etc., preferably in several thin coats. Care must be used to produce a nearly uniform film, especially on edges or in depressions.

Waxes such as common paraffin and beeswax, and stearic acid may be applied to wood or plaster, by heating them to a temperature of about 125°C. (257°F.), *i.e.*, considerably above the boiling point of water. If feasible, the object to be coated is immersed in the melted wax and kept there at the above temperature, until evolution of air or moisture from the pores has practi-

cally ceased. With large objects it may be necessary to paint on the melted wax, and to heat the surface with a hot metal surface or a blow torch. In either case the excess of wax is removed as much as possible, either by scraping or melting it off.

(b) **Rendering Surfaces Conductive.**—In order to render varnished surfaces conductive, an additional coating of varnish or lacquer is applied, and when it is nearly dry, *i.e.*, it is just "tacky," graphite or copper bronze powder is brushed over it very thoroughly. It is also possible to apply (preferably by spraying) over the varnish a conducting paint made by diluting any good cellulose lacquer which is free from gums, such as a silver lacquer, with a suitable thinner. In the thin lacquer there is so little "cotton" (nitrocellulose) that the copper particles are not insulated by it. Sufficient *grease-free* copper bronze powder is then added to produce the desired consistency. If only the ordinary bronze powder is available, it should be first shaken up with some of the thinner, or with ether, to remove the grease. Whenever copper powder or copper lacquer is used, it is advantageous to treat the surface subsequently with a dilute silver cyanide solution (page 157). This causes the deposition of silver by immersion, which slightly increases the conductivity and is useful in detecting spots which are not covered with copper or are insulated. The silver film should not be allowed to dry. Frequently leaves, flowers, etc., are varnished or lacquered, after which (when dry) they are dipped into a dilute solution of silver nitrate and are then subjected to the action of hydrogen sulphide. This produces a thin conducting film of silver sulphide, without danger of injuring the delicate structures.

Wax surfaces, or those which have been coated with wax, may be rendered conductive by simply brushing on graphite (page 164) or copper bronze powder.

Rubber may be rendered conductive by treatment with a copper lacquer, or by coating with wax and graphite or copper powder. Frequently when hard rubber is employed in electrodeposition for insulating purposes it is found that the metal will deposit over the surface of the rubber. This is probably due to the presence in the rubber of conducting "fillers," such as lead sulphide, antimony sulphide, etc., or of absorption by the rubber of salt solutions (*e.g.*, of copper and nickel) which form insoluble conducting compounds with the sulphur of the rubber. This behavior can be prevented by coating the rubber with a thin film of wax.

3. PREPARATION FOR ELECTROTYPING

If we consider the actual process of depositing the metal as the essential step in electrotyping, all the preliminary operations may be considered as preparation. The processes involved are quite different, depending upon whether the deposits are produced upon wax molds or lead molds. Wax molding is most commonly used, as it is the only practical process of obtaining an impression of type forms composed of type metal. Lead molding is applied principally for the reproduction of half tones or cuts, or of electrotypes of type forms, usually in connection with illustrations. The principal advantages of lead molding are the greater accuracy of reproduction (which is especially important in fine half tones) and the fact that the surface requires no treatment to secure the desired conductivity. Various attempts have been made to apply lead molding to regular type forms, but thus far no practical process has been developed.

The essential steps in the wax molding process are as follows: The wax is melted in a steam kettle and is then poured over the "cases," which are plates of copper (or occasionally of lead or aluminum) laid upon a flat rimmed iron bed which forms the top of the "wax table." The layer of wax is about 1/4 to 3/8 in. (6 to 9 mm.) in thickness. Before it solidifies, a flame is applied to the surface, in order to remove any air bubbles. After cooling, the cases are "shaved" by a machine to a definite thickness, and to produce a plane surface. Before molding, if they have become entirely cool, they are warmed slightly, *e.g.*, to about 100 to 110°F. (38° to 43°C.) in a warming closet, usually heated by steam pipes. The surface is then brushed with polishing graphite to prevent the wax from sticking to the type, and the type form, which has also been brushed with graphite, is laid face down upon the wax, and a pressure of about 1,000 lb./sq. in. is applied in a hydraulic press. The molded case is next shaved by a slightly warmed hand knife, to remove the wax forced above the surface. A small flame is then applied to remove any "burrs" and to round the edges of the letters slightly. (The faces of the letters are of course in the bottom of the mold and are not affected by these treatments.)

The mold as thus prepared is rendered conducting by the application of graphite in either a dry form or as an "emulsion." Even when the wet "black leading" process is used, the molds are often first brushed with dry graphite.

In some plants the surface is subsequently treated with copper sulphate and iron filings to secure better conductivity. Contact is usually made between the hanger and the surface by a so-called "face connection." In this method the hooks supporting the case are insulated from the portion of the hanger which makes contact with a small copper plate set in the face of the wax. In the method formerly used a "case connection" was made, in which the metal plate was in the circuit, and if it was exposed at any point through accidental removal of the wax, metal was deposited at those points. The outer portions of the form are "stopped out" by the application of a flame, which destroys the graphite film and thus prevents the deposition upon parts where it is not desired, such as the edges and back of the plate.

(a) Wax Molding.—Many substances have been used in the preparation of electrotypers' wax, especially since about 1916 when the supply of Austrian ozokerite was curtailed. Prior to that time ozokerite was the principal constituent. This is a natural wax found in appreciable quantities in only two localities in the world, Galicia (formerly in Austria but now in Poland), and Utah in this country. It is essentially a mixture of hydrocarbons (compounds of carbon and hydrogen), which differ, however, in constitution from those found in most American petroleum. The most marked difference in physical properties between true ozokerite and paraffin is the much finer crystalline structure of the ozokerite, which is in fact practically amorphous. This difference is attributed to the presence in the ozokerite of a small amount of asphaltic substances. If the latter are entirely removed from the ozokerite, as in the manufacture of ceresin, a more crystalline wax is produced. It is difficult to state the exact chemical or physical properties of a pure ozokerite suitable for electrotyping, because, according to the best available information, the Austrian ozokerite was almost always "compounded" with oils before it was exported from Austria, and possibly again after it entered this country. It is possible, however, that such additions improve the quality of the wax for electrotyping. Even the pure natural product undoubtedly varies decidedly in composition and hardness according as it is mined in different locations or at different levels.

When the supply of Austrian ozokerite was entirely cut off, efforts were made to apply the ozokerite obtained from Utah. This material is found there principally in two forms, one of

which is slightly softer than the imported Austrian wax and the other decidedly harder. Unpublished experiments made in 1916 at the Bureau of Standards by Dr. H. D. Holler showed that by the proper blending of these two waxes a mixture could be obtained which with the customary additions gave satisfactory results.

At present a satisfactory product is being made from American hard ozokerite, by first removing all of the asphaltic material, and then adding a definite amount of the crude wax to introduce the desired trace of asphalt. Sufficient oil is then added to produce the desired hardness and other properties. One advantage of thus "compounding" a wax is that a less volatile oil may be added than is present in the Galician ozokerite. Hence the wax mixture will not change its composition and properties so rapidly when heated.

In the past few years beeswax, which was employed almost exclusively before Austrian ozokerite was introduced, has been again used extensively. Another wax which has been found useful is apimela wax, obtained from a shrub in Texas and Mexico and used as the basis of certain proprietary molding compounds.

In addition to the waxes, almost all molding "compounds" contain rosin or rosin oil, or some similar substances, such as venice turpentine, burgundy pitch, etc. These substances increase the flexibility and ductility of the wax, which in their absence tends to become brittle—especially after repeated heating, which expels some of the more volatile constituents. Small amounts of lampblack or graphite are often added, probably to increase the plasticity. The following are typical commercial formulas of mixtures used when Austrian ozokerite was available.

(1)	Lb.
Pure green ozokerite	100
Parowax (paraffin)	50
Rosin	16
Vaseline in small amounts when necessary to soften wax.	

(2)	Lb.
Brown ozokerite	100
White pine pitch	8
Graphite	2
A mixture of rosin, oil of turpentine, and rosin oil was used occasionally in small amounts to soften the mixture.	

The properties of a successful molding wax have never been defined quantitatively, so that at present a service test is neces-

sary to determine whether a new mixture will prove useful. The hardness of the wax may be used as an indication of suitability. This may be determined by means of the standard penetrometer needle, such as is used in testing asphaltic products. In the above-mentioned tests of Holler, it was found that when tested with a standard needle and a weight of 150 g. for 15 seconds, the hardness of several satisfactory commercial molding waxes at 77°F. (25°C.) ranged from 27 to 33. Even more significant was the ratio between the hardness at 95°F. (35°C.) and at 77°F. (25°C.). The former temperature is approximately that used in the actual molding operation. This ratio for waxes designated as satisfactory by electrotypers was about 2.2; but was considerably above that figure for unsatisfactory waxes. Thus, *e.g.*, a wax made from petroleum residues (probably from "blown oils") had a ratio of over 3 and was entirely unsuitable for molding, as it softened too rapidly when warmed.

More difficult to measure or define is the "plasticity" of the wax. All the evidence shows that a satisfactory wax must be "plastic" and not "viscous." A plastic substance will not flow until a definite appreciable load is applied, while a viscous substance will flow (even though very slowly) just of its own weight. A very simple test serves to distinguish between a plastic and a viscous solid, *e.g.*, between a good molding wax and a sample of pitch. If a piece of each. *e.g.*, 1 cm. (0.4 in.) in diameter and 10 cm. (4 in.) long, is suspended between two edges 7.5 cm. (3 in.) apart, it will be found at the end of 24 hr. or more that the wax has scarcely bent, while the pitch (even if it is much harder than the wax) has been greatly deformed. There is no necessary relation between hardness and viscosity.

It is obvious that electrotypers' wax must not be viscous, otherwise it may flow after molding, and thus lose detail during the operations preparatory to deposition. So far as known, no definite plasticity measurements upon electrotypers' wax have ever been published. Such studies are necessary for accurate prediction of the behavior of any wax mixture.

Another important property of a molding wax is its coefficient of expansion within the working range, *e.g.*, from 20°C. (69°F.) to 40°C. (104°F.). If this coefficient is high, there is a tendency for the wax to crack after casting or after the molding, and also to cause "concave face" on the forms. One of the objections

to beeswax is that its coefficient of expansion is higher than that of ozokerite. This tendency to crack or "concave" is, however, largely overcome by the addition of the resinous substances above referred to.

Another essential property of a good wax is freedom from stickiness, which interferes with proper molding. Excessive additions of rosin or rosin oil tend to increase stickiness, while addition of graphite or lampblack reduces it.

The wax mixture is usually melted in steam-heated kettles preparatory to being poured upon the "cases." In this melting process the lowest temperature should be employed which will keep the mixture in a thoroughly fluid state. The use of higher temperatures causes excessive loss of volatile constituents either of the original wax, or of the resinous additions, and causes the wax to become brittle. It is probably that a temperature of (130°C.) 266°F., which can be secured by steam at a pressure of 40 lb./sq. in., will be sufficient in all cases, and lower temperatures should be employed if possible.

(b) **Graphiting.**—Graphite is used in two steps of the electrotyping process. It is applied in the molding operation to prevent the adherence of the type or engraving to the wax, and to prevent slipping or side movement of the plate during the molding process. Such graphite is known as "molding graphite" or "molding lead."

Graphite is next applied to the wax molds after the "bench operations," just before the molds are introduced into the electrotyping solutions. This application imparts an electrically conducting film to the surface of the wax. The graphite may be either applied dry, (so-called "dry polishing"), or wet, in the form of a suspension in water, commonly, but erroneously referred to as an "emulsion." Dry leading has been largely supplanted on account of a possible health hazard in its use, and of certain mechanical difficulties. In some cases however it is still used prior to the "wet-leading" which is now almost universally employed.

Recently[1] a study of the properties of graphite used in electrotyping was conducted by the Bureau of Standards and the International Association of Electrotypers. The methods and conclusions of this work may be summarized as follows.

[1] Winkler, J. H., and Blum, W., *Trans. Am. Electrochem. Soc.*, vol. 53, p. 435, 1928.

The properties of graphite which determine its usefulness are (*a*) purity, (*b*) fineness and (*c*) conductivity, of which the latter depends largely on the first two.

The purity may be expressed in terms of the carbon content. This is equal to the loss in weight when a dried sample is burned in oxygen. This method does not serve however to detect other forms of carbon such as lampblack that may be introduced as adulterations. Their presence can however be detected from the conductivity as measured in the covering test.

Fig. 23.—Frame Used to Determine the Rate of Covering of Nickel on a Graphited Wax Surface.

The fineness can be determined by the use of standard sieves or screens, *e.g.*, with 100, 200 and 325 meshes per linear inch (or 40, 80 and 130 meshes per centimeter). A weighed sample (10 g.) is placed in the No. 325 screen, mixed with water, and stirred with a camel's-hair brush while a fine stream of water is run through the sieve till practically no more particles pass through. The residue on the sieve is then dried and weighed. This residue is then treated similarly on a 200-mesh sieve. On the 100-mesh screen it is not necessary to use water, as there is no fine dust to be lost in dry screening.

If desired, the content of graphite much finer than the No. 325 sieve can be determined by elutriation with a stream of water that carries out only the finest particles.

The *conductivity* of graphite is often determined for use in dry cells, by compressing the material, at a specified pressure, into a cylinder of definite dimensions, and measuring the conductivity (or resistivity). For electrotyping however the effective conductivity is more readily determined by a covering test.

The *covering time* is determined by measuring the period required for nickel to deposit over a definite area of the graphite film under specified conditions. For this purpose the graphite is applied to a plane surface of wax supported on a hard rubber frame, illustrated in Fig. 23. Contact is made with the graphite film by means of a brass strip connected to a suitable hanger.

The graphite is applied by brushing on to the wax a suspension of graphite in water, and rinsing off the excess of graphite. An area of graphite exactly 2.5 × 15 cm. (1 × 6 in.) is obtained by scraping the edges. A solution containing 0.5 *N* nickel sulphate (70 g./l. or 9 oz./gal. of $NiSO_4.7H_2O$) and 0.1*N* ammonium chloride (5.3 g./l. or 0.7 oz./gal. of NH_4Cl) at a pH of 5.5 to 5.7 is used, at a temperature of 22 to 27°C. (72 to 81°F.). The anode and cathode are 10 cm. (4 in.) apart, and a potential of 3.0 volts is maintained constantly between them. The time required for the nickel to cover the graphite is noted and recorded as the "covering time."

Observations in several plants, together with laboratory tests, led to the following tentative specifications, which are now met by most of the graphites used in America.

Suggested Specifications for Graphite

Kind of graphite	Fineness, minimum per cent through sieve No.			Minimum carbon content per cent	Maximum time of covering minutes	Remarks
	325	200	100			
Dry polishing....	50	75	99	92	8	Time of covering determined dry.
Wet lead.....	50	95	99	92	10	Time of covering determined wet. Shall readily form suspension with water.

It was found that for most purposes the graphite suspensions contain about 2 lb. of graphite per gallon of water, (or 240 g./l. water). Water must be added to replace that lost by evaporation, and graphite to replace that removed with the cases, which is far more than that which adheres permanently to the wax surface. Every few weeks the suspension should be allowed to settle, and the water drawn off and replaced with fresh water. Otherwise impurities such as nickel and copper salts may accumulate and cause corrosion of the metal parts of the machines.

At first it may seem strange that by treating a wax surface which is not itself wet by water, with a mixture of graphite in water, an appreciable amount of graphite should adhere to the

wax. If the wax is similarly treated with a mixture of calcium carbonate (chalk) and water, it will be found that practically none of the calcium carbonate adheres to the wax. The behavior of the graphite is probably due to the difference in surface tension between wax and graphite on the one hand, and water and graphite on the other hand. The conditions are in some respects similar to those existing when carbon is suspended in water and oil, in which case the carbon shows a tendency to go into the oil phase. If we assume that the wax is in effect a solidified oil, its "attraction" for graphite is entirely consistent. That there is a strong attraction is shown by the fact that the graphite adheres to the wax even when subjected to a very powerful stream of water, applied subsequently for the purpose of removing any excess of graphite from the lines and letters. Metallic powders, such as copper bronze powder, behave similarly to graphite.

That the particles of graphite are very thin flakes even when finely divided, is evident from the fact that a film of graphite on wax, when applied dry is only about 0.00002 in. (0.0005 mm.) thick, and when applied wet is only about one-half that thick. These dimensions are much less than the diameters of the finest particles present in the graphites used in these tests.

(c) **So-called "Oxidizing."**—Treatment of the graphited forms with copper sulphate and iron filings was at first used quite extensively as a means of increasing conductivity, and then with the advent of wet "black-leading" the practice was largely discontinued. More recently, however, its use has been revived in many plants, especially in connection with nickel electrotypes. The film of copper actually produced is so thin that it has practically no effect upon the wearing qualities of either the copper or nickel electrotypes; indeed, it is largely removed during the subsequent scrubbing of the plates.

One reason for its use is that, upon a graphited surface without the preliminary copper coating, deposition does not at once take place all over, but the deposit "grows" from the point where contact is made. From 10 to 30 min. is required for a form to "cover" in a nickel solution, and even longer in a copper solution. When a film of copper is produced by the above method, the time of covering is greatly reduced. The slowness with which the graphite film becomes coated with metal may be due to the extreme thinness of the film, and consequent high resistance; or

more probably to the fact that the film is not continuous, *i.e.*, it consists of separate graphite particles, between which the contacts are at best imperfect, and consequently it is necessary for the metal to bridge these gaps before good conductivity is established. In the above tests it was found that a coarse graphite covers more rapidly than a finer powder, probably because there are a smaller number of contacts between the particles. The practical disadvantage of the delay in covering is not only the time involved, but also the fact that the first part of the electrotype "shell" deposited may be appreciably thicker than the last part.

In the so-called "oxidizing" process, the graphited surface is treated with a dilute, slightly acid solution of copper sulphate, and fine iron filings are sprinkled over it and the surface is gently brushed till it is completely covered with copper. In this operation numerous cells or couples are produced, in which each iron particle acts as an anode, *i.e.*, goes into solution and displaces the copper, which deposits upon the graphite film that serves as the cathode. It is therefore a case of electrodeposition in which the energy is furnished by solution of the iron. The term "oxidizing," which is almost universally applied to this process by electrotypers, is not entirely a misnomer, as the iron is in effect oxidized and the copper is reduced.

In special cases metallic copper, in the form of copper bronze powder, is used to produce conductivity upon wax forms, but not to any extent in regular electrotyping, probably because of its greater cost. There is a definite field for the development of cheap effective means of coating wax electrotype forms to render them more immediately conductive than is now possible with graphite.

(d) **Lead Molding.**—The preparation of lead molds is a much simpler operation than that of wax molds. The lead is usually secured in sheets of suitable size, about 0.04 in. (1 mm.) in thickness, and with one side polished and free from scratches. In some cases a special molding lead is used, the finished face of which is covered with a film of tin which is less subject to tarnishing during storage than is the lead. This tinned lead is not suitable for making copper electrotypes, as the tin is readily attacked by the acid copper solution. The lead sheet is either lightly brushed with graphite, or is treated with a very dilute solution of wax or grease in turpentine or other volatile solvent,

in order to prevent it from sticking to the form during the molding operation. Special presses are employed to produce the high pressure (approximately 5,000 lb./sq. in.) which is required in lead molding. The lead mold is usually fastened to an ordinary wax-covered case in order to support it during deposition. In one process, the lead mold is held in a simple slotted frame constructed of bakelite or other insulating material.

In order to permit separation of the subsequently deposited shell, the lead mold may be treated by various means (page 157). The most common practice is to apply a very thin film of sodium (or potassium) dichromate ($Na_2Cr_2O_7$), *e.g.*, about 1 g./1. (approximately 0.13 oz./gal.). This produces a very light film of lead chromate ($PbCrO_4$) upon the surface. Separation can also be effected by the use of a weak solution of sodium sulphide (page 157), which produces a film of lead sulphide. In some cases the lead molds are brushed with graphite to permit separation of the deposit.

CHAPTER XI

ELECTRICAL EQUIPMENT

1. SOURCES OF CURRENT

(a) **Generators.**—Obviously the most essential requisite for electrodeposition processes is a source of low-voltage direct current. As it is not practicable to distribute current to any great distance at as low an e.m.f. as 6 to 12 volts owing to the excessive cost of the large copper conductors which would be necessary to minimize transmission losses, it is customary for electroplating and electrotyping plants to generate their electric power, or to transform it from a commercially transmitted e.m.f., (usually 220 to 440 volts) to that required. In either case, a low-voltage generator[1] is usually employed, driven from a shaft operated by steam power, or by a motor impelled by the commercial current. In the latter case, the shafts of the motor and generator are usually connected together, or the motor is assembled on the generator shaft, forming a "motor-generator set," such as is now used almost universally in the electrodeposition industries.

The fundamental principle of the generator is that when a coil of wire is rapidly rotated in a magnetic field in such a way that it cuts lines of force, a current is produced in the wire. Conversely, when a current is passed through a movable coil placed in a magnetic field, there is a tendency for the coil to rotate to a position in which the maximum number of lines of magnetic force will be enclosed. This latter effect is the basis of the electric motor. In principle, therefore, a motor and a generator may have exactly the same construction. Such an arrangement becomes a generator if the coil is rotated by some external mechanical force, or a motor if a current is passed through the coil by the application of an e.m.f. from an external source. The four most essential electrical parts of a direct-current generator

[1] The word "dynamo," which is frequently, but incorrectly used in place of "generator," is a contraction of "dynamo electric machine," and may therefore refer to either a motor or a generator.

(or motor) are the armature, field magnets, commutator, and brushes. The armature, which carries the moving coils, consists of a cylindrical stack of thin discs of soft steel. The coils of insulated wire are wound in slots running lengthwise of the armature. The field magnets, usually four or more in number, consist of soft iron cores, magnetized by the passage of a current through coils of wire surrounding them so that the inner ends are alter-

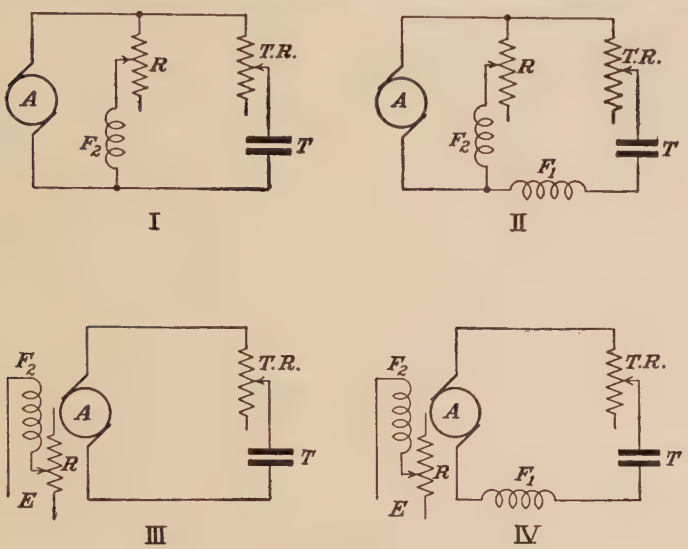


FIG. 24.—Typical Generator Windings.
I. Self excited shunt wound
II. Self excited compound wound
III. Separately excited shunt wound
IV. Separately excited compound wound
A—Armature
F_1—Series field coil
F_2—Shunt field coil
E—Exciter
R—Field rheostat
T. R.—Tank rheostat
T—Tank

nately of north and south polarity. The commutator is the device for collecting and reversing the current. It consists of segments of copper insulated from each other and from the shaft by thin sheets of mica. The terminals of the armature coils are connected to the commutator bars in such a way that as each coil leaves one pole and approaches the next one, which is of opposite polarity, the connections between the coil and the

external circuit are also reversed, and hence the direction of the current outside the machine is the same at all times. The brushes are the terminals of the current leads, which "pick-up" the current from the commutator and transmit it to the leads and thence to the busbars.

The most essential differences in the types of generators used for electrodeposition are in the relation between the current passing through the field and through the armature. The four arrangements which have been used in plating generators are represented diagrammatically in Fig. 24.

The most important consideration in the choice of winding for such generators is the maintenance of a constant voltage when the load in the tanks changes greatly. Any one of the arrangements may yield a constant voltage as long as the load in the tanks remains constant.

The current that passes through the field coils may be derived from the generator itself, in which case the generator is said to be "self-excited." The residual magnetism of the field magnets is sufficient to produce the initial field required to start the generator. In the "self-excited shunt-wound" generator, the field coils are in parallel with the armature, and only a part of the generated current passes through the field coil. Suppose that with such a generator, the amount of work in the plating tanks is increased. This decreases the tank resistance, and the voltage at the generator brushes decreases, due to the increased voltage drop in the armature. The current in the shunt fields therefore decreases and the voltage at the generator terminals drops, and can be maintained only by changing the field rheostat. Such a machine therefore has a "drooping voltage characteristic."

The "self-excited compound-wound" generator has two separate field windings; one of which is in parallel with the armature as in a shunt wound generator, and the other is a winding of low resistance in series with the armature and called the "series winding." As the load in the tank increases, the current through the series winding also increases. This raises the generated voltage. If this just offsets the decrease which would occur with the shunt winding only, the generator has a "flat voltage characteristic." If it more than compensates for the decrease due to the shunt winding, the generator is "over-compounded" and the voltage tends to build up as the load increases. Small machines are generally "self-excited compound wound."

In "separately excited" generators the current required for the field coils is furnished from an outside source, *e.g.*, d.c. current at 110 to 220 volts from a power line, or from a separate small generator installed to furnish the exciting current. The so-called "separately excited shunt-wound" generator is simply a generator in which the entire field current is furnished from outside. Strictly speaking it is not "shunt wound," but the above expression has come into common use, probably in contrast to the term "separately excited compound wound." The latter has a winding of low resistance in series with the armature. As it is difficult to handle very high currents through the series coils, large generators are seldom compound wound. Separately excited shunt-wound generators are most commonly used on large machines. The voltage drop of this type of generator is less pronounced than that of a self-excited shunt-wound generator, but is sometimes sufficient to cause difficulty in maintaining a constant tank voltage. In this case a voltage regulator is advantageous. This regulator automatically adjusts the field current so as to maintain a constant tank voltage, regardless of the load. As it operates upon the small generator that furnishes the current to the main generator fields, it cannot be used except in connection with an exciter.

The type of motor to be employed to operate the generator is determined by the source of current available and by the required power output and efficiency of the generator. If a.c. current is applied, an a.c. motor must be installed, in which case the motor-generator set serves both as a rectifier and transformer. The approximate size of the motor required may be calculated as follows: Suppose that it is desired to operate a generator to yield 2,000 amp. at 6 volts. The power output will then be $2{,}000 \times 6 = 12{,}000$ watts, or 12 kw. If we assume a generating efficiency of 80 per cent, it will be necessary to supply to the generator $100/80 \times 12{,}000 = 15{,}000$ watts. The motor must therefore be able to deliver that amount of power to the generator, *i.e.*, it must be a 15-kw. motor; or (since 1 hp. equals 746 watts) it must deliver $15{,}000/746 = 20.1$ hp. In such a case a 20-hp. motor should usually be installed, unless the generator will be frequently subjected to overloads.

The *power efficiency* of the generator set is equal to the product of the motor efficiency and the generator efficiency. In the above case, if the motor has an efficiency of 85 per cent, the motor-

generator set will have an efficiency of $0.80 \times 0.85 = 68$ per cent. The motor transmits to the generator only 85 per cent of the power furnished to it, and the generator in turn yields only 80 per cent of that amount. In order to secure 12,000 watts, it will therefore be necessary to supply to the motor $100/68 \times 12{,}000 =$ 17,600 watts, or 17.6 kw. or 23.5 hp. The same result is obtained if we calculate from the power requirement and efficiency of the motor, *i.e.*, $100/85 \times 15{,}000 = 17{,}600$ watts. Even though the power consumption represents a very small part of the cost of the electroplating operations, consideration should be given, especially in large plants, to the possible losses arising from defective design or faulty operation of generators. Thus even with the above moderate-sized generator, an increased expense of 5 per cent over a period of 300 working days of 9 hr. each, with electricity at $0.05 per kilowatt-hour, would represent an annual loss of about $119.

The size and number of generators to be used in any plant will depend upon conditions of operation. In those rather unusual cases where continuous operation is essential, it is advisable to provide at least two generators to permit occasional overhauling and repairs. In such an installation each generator should have a current capacity slightly in excess of the normal requirement so that it may not be overloaded when the entire burden is placed upon it. When both generators are available, however, the load should be divided so as to have each operating with a wide margin. Even when continuous operation is not essential, in all plants requiring over 1,000 amp. the expense of two generators is usually warranted by the greater freedom from shutdowns, the ability to take care of "peak loads," and the greater freedom of voltage adjustment. Thus, *e.g.*, in a plant with a maximum requirement of 1,500 amp., much greater flexibility can be obtained with two 1,000-amp. generators than with one 1,500 or even one 2,000-amp. set.

A generator with two commutators is advantageous, in fact it is common practice to design all generators except in very small sizes, with two commutators. Such generators are now built with four terminals, which can be connected in such a way as to give 6 volts or 12 volts, or to give both voltages at once on a three-wire or four-wire system. Such a generator is cheaper and more efficient than two separate generators of the same total power output, and is nearly as flexible, except for the possibility

of shutdowns for repairs. For most cases it will be found preferable to have the two commutators similar, thus, *e.g.*, each generating 6 volts. In special cases it is possible to have different voltages on the two commutators, *e.g.*, 10 and 5 volts. Such an arrangement does not, however, permit the full output of the generator to be secured at any one voltage.

The principal factors in the care of plating generators are the lubrication of the bearings and the care and adjustment of the brushes and commutators. Of the several types of brushes used, those consisting of a mixture of graphite, carbon, and copper, commonly called "metal graphite," are most satisfactory. For plating generators it is necessary to have as low an electrical resistance as possible, and a low friction coefficient. The exact adjustment of the brushes depends upon the machine design, but in any case sparking should be reduced to a minimum. Dust from the air or from the brushes should be blown away from the commutators and armature at frequent intervals. The commutators should be kept smooth and clean and ordinarily should not be lubricated. The formation of a dark shiny film on the commutator generally indicates good operation, and this film should not be removed.

(b) **Storage Batteries.**—The only other source of direct current which need be considered is the storage battery, which may prove very useful to electroplaters for (1) small-scale experiments, (2) electroanalysis of solutions, and (3) occasional plating with gold, silver, or platinum. The principal type of commercial storage battery is the lead peroxide battery, often designated as the lead accumulator or the "chloride accumulator." The Edison battery which contains nickel, nickel oxide and caustic soda solution, is less used but is especially valuable for occasional service, as it does not deteriorate rapidly on standing.

Electrical batteries are usually classified as "primary" and "secondary," which classes are illustrated respectively by the simple Daniell cell and the storage cell. In each form electrical energy is produced as the result of a chemical reaction. The essential difference between the two types of batteries is that in the secondary cells the chemical reaction is reversible, but not (efficiently) in the primary cells. A secondary or storage cell, when charged, is in no way essentially different from a primary cell. When it is discharged (or preferably only partly dis-

charged), it is possible, by the application of a current of opposite direction from an external source, to reverse the chemical action which has taken place, and thus to reproduce the compounds which were present in the originally charged cell. Such a cell therefore serves as a reservoir for electricity, since it is capable of being successively charged and discharged. It is important to note, however, that in such a cell the stored energy is present in the form of chemical compounds, capable of undergoing a chemical reaction which under favorable conditions will produce a current. It is not stored in the same simple sense that electrical energy is stored in a statically charged object such as a condenser.

When fully charged, the ordinary storage cell consists of two kinds of plates or grids constructed of lead and containing in the interstices of the one (the positive plates) lead peroxide (PbO_2), a brown powder, and in the other (the negative plates) a sponge of metallic lead. These grids, arranged alternately, are immersed in an electrolyte consisting of sulphuric acid and water. When this cell is discharged, *e.g.*, by allowing the current to flow between the terminals attached to the two plates, the following reaction in the cell as a whole occurs from left to right:

$$PbO_2 + Pb + 2H_2SO_4 \leftrightarrows 2PbSO_4 + 2H_2O$$

This may be considered as occurring in two steps, thus:

$$PbO_2 + Pb \leftrightarrows 2PbO$$
$$2PbO + 2H_2SO_4 \leftrightarrows 2PbSO_4 + 2H_2O$$

The reactions occurring at the two plates may be represented as follows:

Positive plate:

$$PbO_2 + H_2 = PbO + H_2O$$
$$PbO + H_2SO_4 = PbSO_4 + H_2O$$

Negative plate:

$$Pb + O = PbO$$
$$PbO + H_2SO_4 = PbSO_4 + H_2O$$

In effect, the lead peroxide plate is reduced and the lead plate is oxidized, in each case forming lead monoxide (PbO, litharge), which in the presence of the sulphuric acid forms water and lead sulphate, a white powder. When the cell is

fully discharged, each of the plates is covered with lead sulphate and so much of the sulphuric acid has been combined that the concentration of sulphuric acid in the electrolyte has been reduced, as may be shown by a simple hydrometer reading. For satisfactory operation it is necessary to avoid the formation of "inactive" lead sulphate, as it is difficult to recharge a cell which is badly "sulphated." In every case lead sulphate is formed during the discharge of the cell, but under proper conditions this is in a crystalline form that is readily acted upon during recharging. If, however, the battery is allowed to stand uncharged, the plates become "sulphated," *i.e.*, the lead sulphate is dense and hard and the cell cannot be easily recharged.

When a cell is recharged, the opposite reactions occur, *i.e.*, all the above reactions take place from right to left. There are, however, secondary reactions during both charging and discharging, which therefore reduce the efficiency of the cells below the theoretical 100 per cent.

Storage batteries should never be used to furnish a current above their specified discharge rate, or beyond their rated capacity. When fully charged, the lead batteries should have an e.m.f. of about 2.2 volts, and the electrolyte should have a specific gravity at 25°C. (77°F.) of about 1.28. Distilled water should be added at intervals to replace that lost by electrolysis (evolution of hydrogen and oxygen), but no sulphuric acid should be introduced unless there has been actual mechanical loss. The batteries should never be allowed to discharge below 1.8 volts, and preferably not below 2 volts. In any case they should be recharged at intervals of a few weeks whether they have been discharged or not.

It is a simple matter to recharge batteries by current from an electroplating generator. For each cell to be charged, an e.m.f. of about 2.5 volts is necessary. A generator designed for 6 volts may be used for two cells by adjusting the field rheostat so as to produce 5 volts for two cells; or when the generator is not otherwise in use, it is frequently possible to secure, for the small currents required, an e.m.f. of 7 to 7.5 volts, *i.e.*, sufficient to charge three cells in series. The rate (in amperes) for charging and discharging and the total capacity are specified for each type and size of battery. To prevent reversing the polarity of the generator, a relay should be provided, which opens the circuit if the current is reversed.

2. CURRENT DISTRIBUTION

(a) **Conductors.**—In dealing with small currents derived, *e.g.*, from storage batteries, any ordinary conducting wires may be used. With currents of 100 amp. or more, as commonly used in electroplating and electrotyping, the size of the conductors becomes an important consideration. The two factors which govern the minimum size of conductors are the loss in available potential due to the resistance, and the heating of the conductors. The chief reason for using low-resistance conductors is that the available e.m.f. is usually limited, and if there is an appreciable resistance in the line, this is equivalent to reducing the generator voltage by an amount proportional to the product of the current and resistance, *i.e.*, the "IR drop." Thus if a current of 100 amp. is passed through a conductor with a resistance of 0.01 ohm, the potential drop through this conductor is $100 \times 0.01 = 1$ volt. If, therefore, the e.m.f. at the generator is 6 volts, that at the tanks will be only 5 volts.

The power lost in the conductor is equal to I^2R; therefore in the above case there would be a loss of $100 \times 100 \times 0.01 = 100$ watts. This power is all converted into heat, which is objectionable because of the inconvenience and danger of overheated conductors and because the resistance and hence the voltage loss increases as the temperature is raised. The actual temperature which is reached in the conductor is determined both by the size (or weight) of the bar, by the surface exposed to radiation, and by the temperature of the surroundings.

All the above considerations show the importance of using conductors of the proper material, size, and shape. The only metal that need be considered is copper, since it has the best conductivity of any metal with the exception of silver, and, moreover, it is relatively resistant to acids and alkalis.

The size of the copper conductors should be such that for short runs not more than 1,000, and preferably not over 750, amp. should be carried per square inch of cross-section. Every effort should be made to reduce the length of the busbars, but where for any reason it is necessary to make runs of over 20 ft., the cross-section should be increased so that not over 500 amp. per square inch will be carried. With a run of 20 ft. and return, making 40 ft. in all, with a copper conductor carrying 1,000 amp./sq. in., there will be a voltage drop of over 0.3 volt, *i.e.*, over 5 per cent of that usually generated (6 volts). By doubling

the cross-section so as to carry only 500 amp./sq. in., the voltage drop will be reduced to about 0.15 volt. Where large installations are involved, it is a simple matter to calculate, from the cost of power and of copper, what is the most efficient size of conductors. This is reached when the annual interest on the copper cost is equal to the annual cost of the power lost in the conductors. Heretofore there has been a great tendency in plating and electrotyping plants to use round conductors of annealed copper. Experience shows, however, that flat bars are much better for several reasons. They expose a greater area for radiation; they can be readily mounted on walls; two or more bars can be used to build up conductors of any desired capacity; and they can be readily bolted to each other or to branch bars. Two convenient sizes are 1 by 1/4 in., which will carry up to 200 amp., *i.e.*, as much as is commonly used on a small electroplating tank; and 2 by 1/4 in., which latter can be used to build up conductors of any desired capacity. These bars can be purchased in lengths of, *e.g.*, 20 ft., and used to construct almost any distribution system. Where the bars overlap it is desirable to increase the cross-section, in order to make up for the increased resistance of the joint and of the brass bolts.

The bars on the tanks are required not only to carry the current, but also to sustain the weight of the anodes and cathodes. In such cases hard-drawn copper should be employed, as it is stronger and its resistivity is only slightly greater than that of soft annealed copper. In many plants, especially when the tank bars are very long, brass bars are employed instead of copper. There is no objection to this if the brass bars are large enough to have a resistance no greater than that of copper of the necessary conducting size. Brass is not suitable, however, for acid copper solutions as used in electrotyping, as it may be appreciably attacked and may contaminate the solutions. In most cases the wires used for suspending the work need not be of large size. Simple observation of whether they become appreciably heated will serve as a guide. Copper is usually employed, though the cheaper iron wires may be entirely satisfactory if of proper size, and their use may simplify salvage of the metal deposited upon the wire. Where a large rack is used in electroplating, or a hanger in electrotyping, consideration should be given to the current which it is required to carry, which may amount to 100 amp. or more.

(b) **Contacts.**—Even more important than the size of the conductors is the method of making contacts throughout the circuit. The resistance of a single poor contact may be several times as great as that of the busbars. Wherever possible, therefore, connections between bars, etc., should be made permanent, either by soldering the contacts, or at least by bolting together the cleaned surfaces. It is a common practice to connect bus bars by the use of standard bus bar clamps, which insure a good tight contact without the necessity of drilling holes through the bars. By amalgamating the cleaned surfaces or inserting tin foil before bolting them together a better contact is secured and the joint is protected against corrosion. In a well-designed system it is possible to have (except for switches) continuously soldered or welded lines from the generators to and including the tank bars.

This still leaves possibilities of poor contacts in the anode and cathode hooks. Too often the assumption is made that round tank bars are preferable because by twisting a wire around them, or by supporting a curved hanger upon them, a large contact area is secured. Actually, it will be found that even if, as is usually not the case, both surfaces are very well cleaned, actual contact is made at only a few points. Such a contact is satisfactory provided there is a sufficient mass of conducting metal immediately adjacent. If, then, we wish to assure positive contact at a few points, this can probably be better secured upon bars with sharp edges than upon rounded bars. Thus, *e.g.*, if a hook is suspended upon, or a wire is twisted around, a square bar, it is practically certain to make a good contact on at least two or three points, whereas a few particles of dirt or oxide upon a round bar may cause complete insulation of the wire. Tank bars of hard-drawn copper 3/4 by 3/4in. (19 by 19 mm.) in cross-section have been used very successfully, and will sustain considerable weights on spans of over 3 ft. (92 cm.). For electrotyping, special hangers might be found preferable, but even the regular hanger with a curved section can be used with square bars.

The anode hooks should, wherever possible, be cast, driven, screwed, or soldered into the anodes, so as to make permanent contacts. Copper anodes for acid copper solutions usually have the hook connected to the anode by pouring lead (or type metal) around the hook connection, which also serves to prevent the hook from being dissolved off at the top of the

solution. Nickel anodes are usually supported by copper, nickel, or monel metal hooks. Of these, the pure nickel is least likely to be corroded, and if it is, it will not contaminate the solution. Recently it has been found that anode hooks of acid resistant alloys such as "silchrome" can be used to great advantage, both in nickel solutions and in cyanide solutions. As the resistance of such alloys is high, a fairly large hook should be used. Their use permits complete immersion of the anodes. Unless such hooks are used, it is preferable to have small lugs or projections upon the anodes extending above the solution level.

The switches and fuses employed on the service lines are of the customary types, as the current used (at, *e.g.*, 220 volts) is generally small. On the low-voltage lines, however, with currents amounting often to as much as 3,000 or 5,000 amp., line switches would be quite large and correspondingly expensive. For this reason switches for over 1,000 amp. are very rarely installed, and usually no switches are used on the tanks except in connection with the rheostats. This is entirely satisfactory, since with 6 or even with 12 volts there is very little danger of damage except from a "dead short." This is best guarded against by the installation of fuses or circuit-breakers in the motor circuit, or of circuit-breakers of appropriate capacity in the low-voltage line.

(c) **Rheostats.**—Similarly, it is usually desirable to avoid as much as possible the installation of rheostats in the line to regulate the voltage, as rheostats for over 500 amp. are expensive and troublesome, and are necessarily inefficient, as they do not in any way reduce the power required to operate the motor-generator set. Where more than one kind of work is involved, requiring different tank voltages, it is preferable to regulate the generator voltage by the field rheostat so as to secure the maximum voltage required for any work, and to employ rheostats on each of the tanks requiring lower voltages.

Rheostats are constructed of suitable resistance wire, such as nickel, nichrome, silchrome, constantin, etc. Two types of rheostats are in use, in which respectively the resistance coils are in series and in parallel, represented diagrammatically in Fig. 25.

Suppose that in each case there are five coils, which have resistances of 0.01, 0.02, 0.03, 0.04, and 0.05 ohm respectively,

and that the generator voltage ir 6 volts. Then, disregarding the resistance of the tank and lines, the current secured by various adjustments of the rheostats may be calculated as follows:

In a series rheostat, the resistances at any point will be equal to the sum of the resistances up to that point, *e.g.*, at point 3, the resistance will be 0.01 + 0.02 + 0.03 = 0.06 ohm, and the current will be 6 ÷ 0.06 = 100 amp. By similar calculations it may be shown that for the five steps the currents will be respectively 600, 200, 100, 60, and 40 amp. With the simple form of series rheostat no greater number of adjustments can

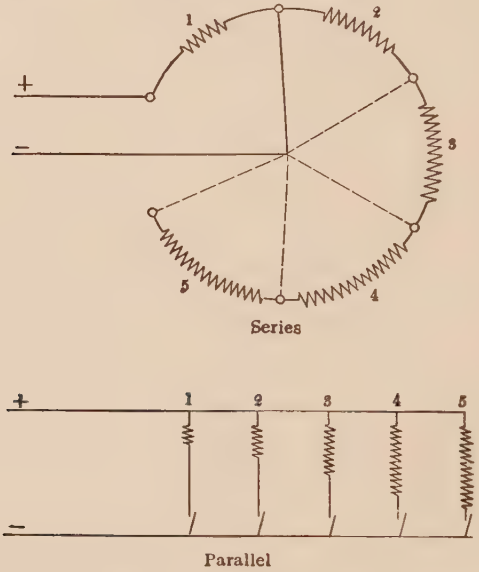


Fig. 25.—Diagram of Series and Parallel Rheostats.

be made than there are coils. By using two moving contacts, greater flexibility may be secured. It should be noted that with series rheostats, as more coils are put into circuit, the current is decreased. Therefore, the coil of lowest resistance must be large enough to carry the maximum current desired.

In a parallel rheostat the resistance is decreased, and therefore the current is increased, as additional coils are introduced into the circuit. Hence all the coils are in use when the maximum current is to be carried. The number of adjustments is equal to the number of combinations that can be made. It is possible by means of five coils, with resistances in the proper

ratios, to secure a large number of adjustments between the lowest and highest resistances. It will be recalled (page 58) that the resistance of two or more coils in parallel is less than that of either of the single coils. The reciprocal of the total resistance is equal to the sum of the reciprocals of the separate resistances, or $\frac{1}{R} = \frac{1}{R_1} + \frac{1}{R_2} + \frac{1}{R_3}$ etc. This can be more readily recalled if we remember that the conductance is equal to the reciprocal of the resistance. It is quite obvious, therefore, that if two coils of equal conductance are in parallel, the current can pass twice as readily as through one coil; in other words, the conductance is equal to the sum of the two separate conductances.

With parallel coils having the resistances above specified, the current which will pass when any one coil is in circuit is equal to the e.m.f. (in this case 6 volts) divided by the resistance of that coil, therefore respectively 600, 300, 200, 150, and 120 amp. Suppose now that coils 1 and 2 are in the circuit, then the resistance and current can be calculated thus:

$$\frac{1}{R} = \frac{1}{R_1} + \frac{1}{R_2} = \frac{1}{0.01} + \frac{1}{0.02} = 100 + 50 = 150$$

therefore

$$R = \frac{1}{150} = 0.0067$$

$$I = \frac{E}{R} = \frac{6}{0.0067} = 900 \text{ amp.}$$

With a given e.m.f. (omitting the tank resistance), in a parallel rheostat the current carried by the two coils is equal to the sum of that carried by each of the coils separately. The resistance of the coils should therefore be selected so as to yield conductances (and not resistances) which can be added together like the weights in a set. Instead of leaving the resistances in the ratio of 1, 2, 2, 5, 10, etc., their reciprocals should be in such ratios. The resistances will then be in the proportion of 1, 2, 5, 5, 10, etc.

A very simple form of parallel rheostat for experimental work, with commercial current of 110 or 220 volts, can be made by arranging a "bank" of incandescent lamps in parallel. No switches are necessary, as the lamps can be screwed in or out as desired.

Another form of rheostat which is useful for experimental work is the "carbon rheostat," which consists of plates of carbon in a frame with a screw for adjusting the pressure. The resistance is decreased by screwing the plates closer together and vice versa. The carbon rheostat has the advantage of permitting continuous instead of stepwise adjustment, but the disadvantage is that the resistance changes decidedly if the plates are shaken or disturbed, or if they become heated by the passage of heavy currents. For general use, therefore, parallel rheostats, such as can be readily constructed from suitable coils and switches, are preferable. If it is desired to cut out all resistance in the line, a separate switch must be provided to short-circuit the rheostat.

3. CURRENT MEASUREMENT

(a) **Electrical Instruments.**—The purpose of an *ammeter* is to measure the current flowing in a circuit at any given instant,

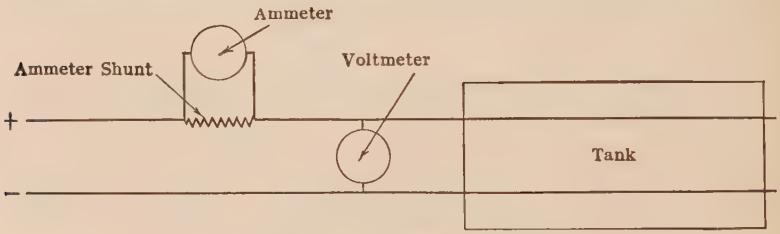


Fig. 26.—Position of Ammeter and Voltmeter.

while a *voltmeter* is used to measure the potential difference between two parts of a circuit. Both instruments depend upon the same principle, that when a current is passed through a coil of wire surrounding the core of a fixed permanent magnet, the coil tends to rotate. If this rotation is opposed by any force, such as a spring or the torsion in a wire, or by gravity, the angle of rotation is determined by the number of turns in the wire, and the current passing through it. With a given coil of definite resistance, the rotation of the coil, as indicated by a needle attached to it, may serve as a measure of the current or of the voltage, since the magnitude of the former is determined by that of the latter. There are two principal types of instruments used. In the D'Arsonval type the magnet is fixed in position and the coil is free to move on an axis; while in the "soft iron" type, the coil is fixed in position and the piece of soft iron is

moved by the passage of the current. The latter instruments are cheaper but somewhat less accurate and reliable than those of the D'Arsonval type, and are therefore rarely used.

The essential difference between an ammeter and a voltmeter as actually constructed is that the ammeter has a very low resistance and the voltmeter a very high resistance (up to several thousand ohms). The reason for this difference is clear if we consider the positions in which these instruments are placed in a circuit (Fig. 26). The ammeter is always placed in series with the tank, *i.e.*, in the main circuit, so that all the current passes through it or, as will be explained later, through it and the shunt connected with it. If, therefore, the ammeter (including the shunt) has a resistance comparable with that of the tank, it will materially reduce the current passing through the latter. Its resistance is hence made very low by the use of a few coils of relatively large wire. The voltmeter, on the other hand, is always connected across the tank, *i.e.*, in parallel with it. In such an arrangement, if the voltmeter has a low resistance a relatively large proportion of the current will pass through it, and hence be deflected from the tank. For this reason the voltmeter usually has a coil consisting of a large number of turns of fine wire.

If an appreciable current were passed through the ammeter coil, it would produce excessive heating. It is customary, therefore, to pass only a definite part of the current through the coil. This is accomplished by arranging, in parallel with the ammeter coil, another coil or shunt, of lower resistance, which bears a definite ratio to that of the ammeter coil. Thus if the two resistances are in the ratio of 9 to 1, 9/10 of the current passes through the shunt. The graduations on the ammeter scale will in that case be so numbered as to indicate 10 times the current which actually passes through the ammeter coil and therefore to denote the entire current to be measured. For portable instruments of moderate range, such shunts are often contained in the case with the ammeter; but for larger ranges, outside shunts are provided which are connected in series in the main circuit in which the current is to be measured. These shunts are simply conductors of definite resistance, to the ends of which the ammeter leads are attached. Since the accuracy of the readings depends upon the ratio of the resistance of the shunt to that of the ammeter including the leads, the latter should not be ex-

changed or altered in length. For small currents, ammeters are often provided with three ranges, *e.g.*, 1.5, 5, and 15 amp., secured by means of appropriate self-contained shunts, and corresponding binding posts.

The great similarity between an ammeter and a voltmeter may be illustrated by the fact that they can be used interchangeably, with proper adjustments. Thus a sensitive voltmeter (*e.g.*, a millivoltmeter) may be used to measure the current passing through a copper bar of definite cross-section, by simply applying the two terminals to points a definite distance apart on the bar. Suppose that the terminals of a millivoltmeter are applied to two points 12 in. (30 cm.) apart on a round copper conductor 1 in. (2.5 cm.) in diameter. Such a bar has a cross-section of 1,000,000 "circular mils."[1] From a table of conductivities, such as are given in many electrical handbooks, it will be found that the resistance of 12 in. of such a bar is approximately 0.00001 ohm. If, therefore, the potential drop indicated by the millivoltmeter is 0.002 volt (2 millivolts), the current may be calculated:

$$I = \frac{E}{R} = \frac{0.002}{0.00001} = 200 \text{ amp.}$$

Even when it is not important to know the exact current on a given bar, such measurements may be very useful in determining quickly whether the same current is flowing through each of several bars or tanks. To make these measurements it is convenient to have the two voltmeter leads attached to a small board, so that the wires make contacts at a definite distance apart (*e.g.*, 12 in.). This method may be used to measure the actual or relative currents flowing on any bars, without disturbing the connections in any way.

In any case, measurement of the current on a tank or even on a given bar indicates only the rate of flow of electricity, and not the *current density*, which is the factor which determines the rate of deposition in any tank. This can be approximately calculated if the area of the work is known. With complicated shapes it is, however, difficult to compute this area, and where racks are used their areas must also be taken into account. Even

[1] A circular mil is defined as the area of a circle 0.001 in. (1 mil) in diameter. A round bar 0.5 in. (500 mils) in diameter has a cross-section of 500 × 500 = 250,000 cir. mils.

when all these calculations are made, the result gives only the *average* current density and is no indication of the actual thickness of deposit upon different parts of an object. With irregular shapes or objects with deep recesses the current density and thickness of deposit may be more than five times as great on some parts as on others. It is partly for these reasons that the ammeter is not more generally used in electroplating. It is possible to reproduce current conditions on a given class of work simply by regulation of the voltage, *provided* the composition of the solution, the temperature of the solution, and the anode and cathode areas and polarizations remain constant. Such an assumption is, however, never warranted, and therefore the ammeter and voltmeter should both be used to insure uniformity of operation.

In the effort to measure the actual current density in the tanks, an instrument known as the "foot-ampere meter" has been devised by E. Heil. This consists of a piece of metal having a definite area (*e.g.*, 0.2 sq. ft.), which is suspended from the tank bar in such a way that the current passes through a small ammeter. The graduations are so adjusted that the current density in amp./sq. ft. may be read directly. This instrument may be suspended from the bar at any point in the tank, and will then give an *indication* of the cathode current density at that point. It may prove very useful for detecting *variations* in current conditions in different tanks, or in different parts of a tank, or on different days, but, for reasons above stated, it does not measure the actual current density that would be produced on an article of entirely different shape hung in the same relative position in the tank.

Where it is desirable to measure and control with considerable accuracy the actual weight of metal deposited, as, *e.g.*, in silver or gold plating, this can be accomplished by means of an "ampere-hour meter." This measures the actual quantity of electricity that passes in a given interval. In many cases the ampere-hour meter for electroplating is so devised that a bell is rung when a certain number of coulombs have passed. It is important to remember that this instrument measures the quantity of electricity and not the weight of metal deposited, which is proportional to it only if the cathode efficiency remains constant. Thus if on two different days, owing to differences in the temperature or composition of the solution, or to a change in current density, the cathode efficiency of a silver bath is 90 and 99 per

cent respectively, there will be 10 per cent more silver deposited on the latter day than on the former by the same quantity of electricity, as measured by an ampere-hour meter. The instrument does not, therefore, insure a definite weight of metal even when so calibrated, though it does aid in securing uniform results. Actually, however, the cathode efficiencies in silver baths are so nearly 100 per cent that no appreciable error is likely to occur. In chromium plating the cathode efficiency varies so greatly with the current density that readings with an ampere-hour meter give only an approximate indication of the weight or thickness of chromium deposited.

Where it is desired to determine the cathode efficiency in an electroplating bath, this may be calculated approximately by weighing the cathodes before and after plating, and noting the current and period of plating. Any such results are, however, only a rough approximation, due to the possible fluctuations in the current strength, or to errors in the ammeter calibration, the measurement of the time, and the accurate weighing of the cathodes. For such purposes it is therefore preferable to make observations upon a smaller scale, using a copper (or silver) coulometer (page 62) to measure the quantity of electricity.

4. LOCATION OF EQUIPMENT

In the installation of electrical equipment in a plating plant, it is often necessary to compromise between the considerations of protection and convenience of equipment. At best, the atmosphere of a plating plant is certain to have a high humidity, and more or less acid fumes or alkaline spray. It is therefore necessary to protect the generators and instruments so that they may preserve their efficiency and accuracy. If, however, this effort at preservation results in the location of the generator where it is inaccessible and is therefore neglected, or of the ammeters at a point where they are never consulted, more harm than good is accomplished.

The generator should be mounted on a solid base, preferably of concrete, and should be bolted rigidly in place. It should be as close to the plating tank as is feasible, and preferably at a point intermediate between the tanks, so as to avoid excessively long busbars. It should be protected as much as possible from dust and fumes, and should be provided with good ventilation, either from a window or by a fan. In many cases these condi-

tions may be met by housing the generator on one side of a plating room, with a wood and glass partition around it. The occasional practice of supporting a generator near the ceiling is questionable, as it is thereby made inaccessible, and is also subject to the action of the heated vapors which rise toward the ceiling. By placing the generator upon a concrete base, raised, *e.g.*, 6 in. above the floor level, it is protected against damage from spilled solutions, overflow of water, etc.

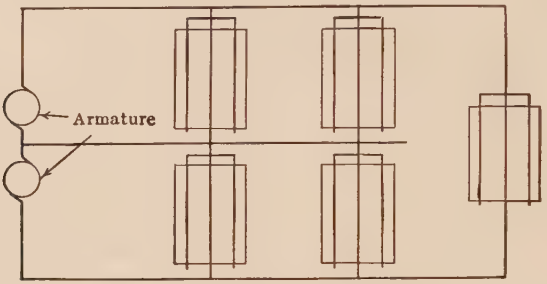
The starting switches, circuit-breakers, field rheostat, and main voltmeter and ammeter should be located upon a switchboard close to the generator but facing the plating room. Thus, *e.g.*, the switchboard can be made a part of the partition of the generator housing. The tank rheostats, voltmeters, and ammeters are preferably located close to the tanks, so that they may be read or adjusted as work is introduced or removed. Where a considerable number of tanks are placed close together it is sometimes convenient to have the voltmeters and ammeters mounted upon a single switchboard, which may be the same as that for the generator. In such a case it is possible to use a "multiple switch" for the voltmeter, by means of which the voltage on each tank may be read. If the generator is working at nearly its full capacity, a change in the load on one tank may change the generator voltage and thus necessitate adjustment of the field rheostat or of the other tank rheostats. This can be accomplished more readily if all are on one panel board.

The busbars from the generator to the tanks are usually run overhead. Where the plating room is located above the basement floor, it is often an advantage to run the busbars down through the floor and along the ceiling of the room beneath. Connections to the tanks are then made through water-proofed openings in the floor. If the latter is of cement, the openings may be surrounded by a ring of cement. If wooden floors are used, asphalt may be placed around the duct through which the bars pass. In any case they should be as completely accessible as possible. Two advantages of running below the floor are that usually the distance is thereby shortened, and the space above the tanks is more free. This is an especial advantage where mechanical conveyors of any type are to be used, as is often feasible in large plants.

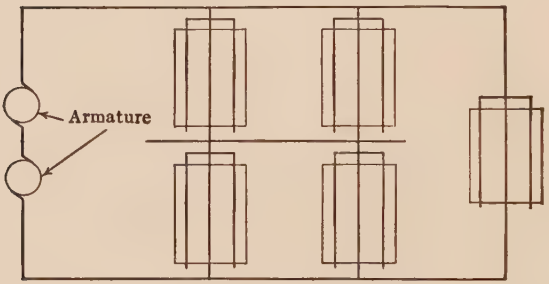
In practically all electroplating plants the tanks are arranged in parallel. Such a plan is justified by the fact that there is

seldom sufficient work of a similar size and shape to permit that balancing of cathode areas which is necessary for successful series operation. As the actual e.m.f. required in many plating baths is not over 3 volts, it is possible to operate two tanks in series with the customary 6-volt generator, but not usually practicable for the above reason.

In electrotyping plants it is customary to operate two acid copper tanks in series. This is possible because the forms are



Two and Three Wire System



False Neutral System

FIG. 27.—Typical Tank Arrangements for Two Armature Generator.

usually of similar size, or at least of only a few sizes, and the voltage required to produce current densities even from 50 to 75 amp./sq. ft. (5.5 to 8 amp./dm.^{2}) is usually less than 3 volts. In unusual cases, where the work is very uniform and where solutions of high conductivity and large copper conductors are used, it is possible to operate three acid copper tanks in series on a 6-volt generator and secure 50 amp./sq. ft. (5.5 amp./dm.^{2}). This practice is not, however, adapted to general conditions.

Where a considerable variety of work is involved, as in a plating plant requiring, *e.g.*, 5 volts on plating tanks and 10 volts on plating barrels, or in an electrotyping plant operating copper tanks at 3 volts and nickel tanks at 6 volts, it may be advantageous to employ the three-wire system, which is based upon the use of a generator with a double commutator. In this system, as shown in Fig. 27, it is desirable approximately to balance the currents used on the two sides of the line but not so closely as in a simple series arrangement. A slight modification is made in the "false neutral" system also illustrated in Fig. 27.

CHAPTER XII

TANKS AND THEIR EQUIPMENT

Under this heading may be considered the apparatus used for preparing, containing, and operating plating solutions. The first consideration is the material of which the tanks are to be constructed, which in any given case is determined principally by (1) resistance to attack by the solutions concerned, (2) mechanical strength for the loads involved, and (3) cost, including investment, upkeep, and depreciation. Other factors, such as electrical and thermal conductivity, may also influence the choice of materials.

1. MATERIALS OF CONSTRUCTION

The materials that have been used or suggested for the construction of plating tanks include wood, iron (or steel), stoneware, concrete, and soapstone; and for small or experimental tanks, glass, enameled iron, and hard rubber. No one of these materials possesses all the desired properties. Their relative advantages and disadvantages will be discussed in the light of the above-mentioned considerations. For general purposes we may consider all the solutions as either (*a*) nearly neutral, *e.g.*, water and nickel plating solutions; (*b*) acid, *e.g.*, pickles and acid copper solutions; and (*c*) alkaline, *e.g.*, cleaning solutions and cyanide copper, brass, or silver plating solutions. Where the materials do not possess the desired chemical resistance, appropriate linings will be considered.

(a) **Wood.**—In the past by far the greatest number of plating tanks were constructed of wood, lined if necessary with other materials. This general use of wood was due not so much to its cheapness or special fitness for the purpose, as to the fact that it is usually accessible and can be fabricated by mechanics with customary training and equipment. Wood is not as resistant to the action of solutions as are many other substances, and with present lumber prices a well-made wooden tank may cost as much as one made of other materials.

The essential constituent of wood is cellulose, a substance which is not appreciably acted upon by either dilute acids or alkalis. The disintegrating action of such solutions upon wood is therefore due primarily to the removal of the constituents which bind the fibers together. (In the manufacture of paper pulp from wood, hot solutions of alkali or of salts are used to remove the constituents other than cellulose.) The desirable properties of wood for plating tanks are therefore impermeability and freedom from readily soluble constituents. The woods which have been found most satisfactory are cypress and redwood, both of which are extensively used.

The initial action of solutions upon wood results in the extraction from the wood of certain constituents, such as tannins (from oak or chestnut) and resins (from pine, etc.), the removal of which not only weakens the wood but may also result in serious contamination of the solutions. Where wooden tanks are to be used without linings, it is therefore advisable to soak them for several days with a solution of similar reaction, *e.g.*, with water or with dilute sulphuric acid, and to discard this solution.

The life of a wooden tank depends largely upon its construction. It is necessary to use good workmanship to insure tight joints, which are usually "tongue and grooved." The tanks should be reinforced not only with brass bolts at the ends but also with rods running through the boards at intervals of 18 to 24 in., *e.g.*, one in each end and three in each side and three in the bottom of a tank 3 by 6 by 3 ft. deep. The thickness of the boards will depend principally upon their length, *e.g.*, for a length of 3 ft. or less, 2-in. stock will suffice; for 3 to 6 ft., 3-in. stock is used. As most plating tanks are not over 3 ft. deep, there is not much hydrostatic pressure developed.

(b) **Linings for Wood.**—For water or for nearly neutral solutions, *e.g.*, nickel plating baths, wooden tanks can be used without any linings. This practice has the advantage of keeping the boards wet and swelled, thus maintaining tight joints. For acid solutions they must, however, be lined with some "acid-proof" material. Wooden tanks are not suitable for strongly alkaline solutions even when lined, as the wood is readily attacked by even occasional contact with alkali. All wooden tanks should be painted on the outside, preferably with a bituminous paint.

For many purposes bituminous linings prove very satisfactory. Either asphalt, tar, or petroleum products may be used

successfully. For this purpose the material should have a melting point of at least 200°C. (390°F.), it should not soften or flow at temperatures up to 75°C. (135°F.), and it should be hard but not brittle at ordinary temperature. It should be applied in a melted condition, either by means of swabs or by pouring it on the surface and spreading it with a suitably sized board. The tanks should be first cleaned and dried and a coat of a bituminous primer applied with a brush. Such a primer can be purchased, or can be made by dissolving some of the solid bitumen in benzene (benzol). The priming coat should be allowed to dry to a slightly "tacky" condition before applying the hot asphalt or tar.

For weakly acid baths, the inside of wooden tanks may be painted with "bakelite," which is a proprietary phenol condensation product.

Another type of lining which has been suggested, but not extensively used, is made of rubber, applied to the wood in such a way as to adhere firmly. As rubber is flexible and not readily attacked by dilute acids, such linings may prove very useful for electroplating tanks. It is not suitable for strongly alkaline solutions, as these may extract sulphur from it.

For acid copper solutions used in electrotyping, lead-lined tanks are extensively employed. Such a tank is in effect a lead tank supported by the wooden tank. The lead should be fairly thick, at least equal to "6-lb. lead" (weighing 6 lb. per square foot), which is approximately 1/10 in. (2.5 mm.) in thickness. It must be united at the joints and corners entirely by "lead burning," which is accomplished by melting the edges together with a blowpipe, an operation requiring great skill and experience. Where tanks are over 3 ft. deep, it is desirable to anchor the lead to the walls at several points. In any case it should be fastened along the top edges by brass screws. As the lead is scarcely attacked by dilute sulphuric acid, it makes a very durable though rather expensive lining. Its chief disadvantage is its electrical conductivity which gives rise to occasional short circuits, which cause not only a loss of current, but also result either in deposition of metal on the linings, or in the liberation of acid in the solution, according to whether the lining becomes the cathode or anode. For this reason it is customary in electrotyping plants to cover the lead lining with a thin wooden or bakelite lining, which serves only to prevent the electrodes from

touching the lead. Efforts to coat the lead with a bituminous covering have not been very successful, as the coating tends to peel off and expose the metal.

(c) **Iron and Steel.**—For alkaline solutions, iron or steel tanks are almost exclusively used. They should be of heavy gage metal, as otherwise they are readily deformed or may be eaten through by corrosion from the outside. They are usually welded, either by means of acetylene or by arc welding, preferably with a double lap weld. The principal precaution to be observed in this welding is that the metal should not be "burnt," *i.e.*, there should be no oxide inclusions in the weld. Iron oxide may be readily dissolved by alkaline cyanide solutions, especially when, as in electrolytic cleaning, the tank is made the anode. In several cases leaks in iron tanks have been traced to the presence of oxide in the welds. Iron plating tanks possess the same disadvantage as lead, of being conducting and therefore tending to cause short-circuits. This conductivity, however, is frequently utilized in electrolytic cleaning, by making the tank serve as the anode.

Recently rubber-lined steel tanks have been very successfully used for nickel plating and acid copper plating baths, and for acid pickles, such as hydrochloric or sulphuric acid. This development has come about largely as the result of great improvements in the adherence and quality of rubber linings.

For chromium plating, steel tanks are generally employed. Occasionally they are used without linings, under which conditions however, considerable iron may dissolve, especially if the tank becomes anodic. For this reason it is a common practice to insert loosely, linings of reinforced glass. Lead-lined iron tanks are also extensively used for chromium plating, in some cases with an additional glass lining.

Fused glass-lined tanks, such as are used in many chemical operations, are also satisfactory for chromium, silver and gold plating baths.

(d) **Stoneware.**—Vitrified stoneware is very resistant to dilute acids, and may therefore prove useful for plating tanks. It is usually glazed, but stoneware of high quality does not depend upon the glaze for resistance to acid. It is attacked, however, by hydrofluoric acid. In most cases where hydrofluoric acid is used in plating solutions, *e.g.*, in lead and occasionally in nickel solutions, it is combined with boric acid to form fluo-

boric acid, which has only a very slight action on stoneware. For such solutions, however, the stoneware should be coated with asphalt as a precaution. For small installations, *e.g.* up to 100 gal., stoneware tanks are very satisfactory for chromium plating.

Stoneware is slightly attacked by dilute alkalis, and markedly so by strongly alkaline solutions, and is therefore not suitable for use for cleaning solutions. The chief advantages of stoneware tanks are their resistance to the chemical action of many solutions, their low electrical conductivity, and high thermal conductivity. The latter property is an advantage when it is necessary to keep the solutions cool, *e.g.*, in summer. Their principal disadvantage is their relative fragility and consequent danger of breakage in transit and in use. The latter danger can be minimized by the use of suitable wooden guards at corners where they are likely to be hit.

(e) **Concrete.**—Reinforced concrete tanks have been used occasionally for plating and electrotyping. They can be built of cheap, readily available materials, and in any size or shape that may be desired. They are, however, not usually portable, and must therefore be destroyed if the plant location is changed. Concrete is not very resistant to acids and alkalis, and consequently the tanks must be lined, *e.g.*, with asphalt. They also are subject to cracking from heavy impacts.

(f) **Soapstone.**—A variety of soapstone, known as "alberene," has been employed very largely for sinks used in chemical laboratories. This material when free from imperfections is fairly resistant to dilute acids and alkalis. The chief difficulty in its use for plating tanks is that of securing satisfactory joints. These are usually formed by means of metal dowel pins, and a cement (*e.g.*, litharge and glycerin) is used to fill the cracks. Such a cement is likely to be attacked by continued exposure to acids or alkalis. If attacked, the result is not only leakage of the joints but also exposure of the metal dowel pins, which then corrode and by expansion crack the stone. If alberene tanks are used, the joints at least should be thoroughly coated with a bituminous material.

(g) **Glass, Hard Rubber, and Enameled Iron.**—For small experimental tanks, *e.g.*, up to 1 gal. (4 l.), rectangular glass battery jars are most convenient. They are reasonably cheap, practically unacted upon by acids or alkalis, and permit observa-

tion of the position and condition of the electrodes. If heated gradually, they can be used to contain hot solutions, although at times they are poorly annealed and may crack most unexpectedly. Even for larger sizes they are very useful, but the danger of breakage is greater. For this reason hard rubber battery jars are sometimes preferable. They are quite resistant to acid solutions, but not to alkaline. They soften at high temperatures and cannot, therefore, be used safely at temperatures much above 40°C. (104°F.). Enameled iron has practically the same resistance to acids and alkalis as has glass, but has the disadvantage that after long use the enamel is likely to chip off. Vitreous enameled iron tanks are extensively used for gold and platinum plating.

Greater consideration should be given to the size of plating tanks. In general, it is desirable to have them as large, and especially as deep, as conditions justify. A large volume of solution is advantageous in reducing the effect of changes in concentration or composition which may occur during the operations. A relatively deep plating tank is desirable because it facilitates the settling of suspended matter. The added investment for the larger volume of solution required in large or deep tanks is usually justified.

2. INSULATION

In any case, but especially when using metal or metal-lined tanks, it is necessary to use some insulating material to support and separate the busbars along the edge of the tanks. Except for the presence of moisture or of the solutions, there would be no difficulty in securing suitable material, as with an e.m.f. of only 6, or at most 12, volts, there is little chance for *direct* electrical leakage. The principal difficulty is that of securing insulating materials which will not absorb or be attacked by the solutions. If the insulating strips become impregnated with the solutions, they become *electrolytically* conducting. Under such conditions there is not only a loss of current but also an attack of the busbars. The most common practice is to use wooden strips or blocks, and to replace them when they show disintegration. It is advantageous to impregnate the wood by dipping it into heated wax or asphalt. Frequent coating with shellac also prolongs the usefulness of the wood. Other materials are, however, preferable to wood. Hard rubber and bakelite are

very suitable, and the greater expense will probably be balanced by the increased resistance to attack. Stoneware strips or tiles and porcelain tiles are resistant but somewhat fragile and subject to chipping if hit by the heavy anodes. Alberene stone resists neutral or slightly acid solutions, but when subjected constantly to conditions which permit the concentration of acid solutions by evaporation, it is rapidly disintegrated. Glass is satisfactory in all respects except its fragility. There is need for the development of an inexpensive insulating material which will be non-absorbent and will resist the action of acids and alkalis.

In connection with insulation it is important to prevent any pipes used in the tanks from getting into the circuit. This can be most readily accomplished by connecting each pipe with an insulated joint, consisting of hard rubber. A simple insulated joint consists of a few inches of rubber hose, which must, however, be frequently replaced if exposed to steam.

In recent years the need for insulating certain parts of the plating racks has arisen, especially in connection with automatic plating and with chromium plating. In such cases it is desirable to avoid the loss of current and of metal upon the rack itself. In principle the rack should be insulated entirely, except where it makes contact with the cathode bar and with the articles to be plated. The ideal insulating material for this purpose should resist both alkalis and acids as well as the plating bath, so that the racks can pass through the cleaners and pickles without injury. No material fully meets these requirements, but for many purposes rubber coatings are most satisfactory. They are however, attacked by strong alkalis and by chromic acid. For chromium plating, phenol-condensation products such as bakelite have been proposed. They are however slowly attacked and thus increase the content of trivalent chromium in the baths. Ordinary nitrocellulose lacquers are also fairly resistant to chromic acid. Vitreous enamel resists moderate concentrations of most acids and alkalis, but is so brittle that cracks soon develop and permit corrosion of the underlying metal.

In connection with insulation, the "stopping off" of certain areas of the cathode may be considered. This procedure is especially useful in producing thick deposits, *e.g.* in building up certain surfaces, or in electroforming. No single substance is suitable for general use in acid and alkaline baths and in hot and cold solutions. Up to temperatures of about 40°C. (104°F.)

certain waxes such as paraffin and ozokerite are generally useful, and higher melting paraffin can be obtained now. Their adhesion to metal surfaces can be increased by the addition of a small amount of a resin. For acid solutions bituminous coatings are quite useful and can be obtained with relatively high melting points, *e.g.*, above 100°C. (212°F.). Bituminous paints or enamels, especially after baking, are more resistant but more brittle, and may be difficult to remove subsequently. Nitrocellulose lacquers are useful for stopping off in chromium plating, and may be colored to better define their area. In all cases these "stop-offs" should be applied if possible after the metal surface has been cleaned, as otherwise they may be removed by the cleaning solution.

3. AGITATION

(a) Air Agitation.—It is frequently desirable to agitate depositing solutions, thereby insuring uniformity of composition and permitting the use of higher current densities than would otherwise be possible. In electrotyping this is accomplished by means of compressed air delivered through perforated lead pipes, preferably so placed as to have the maximum degree of agitation between the anodes and cathodes. Where air agitation is used it is essential that the air should be freed from oil by means of suitable traps or washers, as even very faint traces of oil in these solutions may be detrimental. Air agitation has the advantage of adaptability, as it can be introduced into any part of the tank, and the degree of agitation can be controlled by simple valves. The disadvantage is that by the introduction of air an oxidizing atmosphere is maintained in the solutions, and secondary (and possibly deleterious) chemical reactions may be accelerated. Thus it is well known that the use of air agitation in acid copper solutions is in part responsible for the consumption of sulphuric acid and the accumulation of copper sulphate which almost always occur. This effect is accounted for by the fact (page 211) that there is a tendency for the copper to pass into solution in the cuprous state (Cu^{+}), and the oxidation to the cupric state (Cu^{++}) is fostered by the presence of oxygen. Aside from the accumulation of copper sulphate (which may prove very troublesome) there is no definite evidence that the use of the air agitation is detrimental in such solutions. It is possible with air agitation to secure high cathode efficiencies and to produce dense copper

deposits of desirable physical properties. With other metals, such as lead and zinc, however, air agitation results in distinctly inferior deposits. With nickel, the effect of the air is uncertain. This form of agitation is used very generally in nickel electrotyping baths with beneficial results, but in electroplating and even in electrotyping with some solutions, such agitation is apparently harmful. As electrodeposition at the cathode is essentially a process of chemical reduction, the maintenance in the solution of oxidizing conditions appears, on general principles, to be contradictory. Air agitation is occasionally used in chromium plating, especially to equalize the temperature in the bath. It probably reduces the cathode efficiency. Air agitation in cyanide solutions is objectionable because it increases the formation of carbonates, both through oxidation and through absorption of carbon dioxide. Much work remains to be done upon the effects of air in plating solutions.

(b) **Mechanical Agitation.**—Mechanical agitation of solutions on a commercial scale often involves practical difficulties. It may be accomplished either by movement of the anodes or the cathodes, or of the solution by stirrers not in the circuit. Where the cathodes are circular or symmetrical, they can often be rotated as, *e.g.*, is commonly done in the plating of auto lamp reflectors. If the cathode is a hollow cylinder, it is often possible to rotate the anode within the cathode. This has been done successfully in lead plating the interior of ordnance shells. In some cases, as in plating spoons, the cathode rods are moved mechanically. Where, however, the cathodes are large and flat or of irregular shapes, it is difficult to move them rapidly, or even to move the solution adjacent to them. If the latter operation is accomplished by means of moving stirrers or paddles, difficulty is experienced in securing materials which will not be attacked by the solutions. Wood or hard rubber are most commonly used for this purpose.

Whatever method is used for agitation, there is danger of particles from the anodes being kept in suspension and giving rise to roughness on the cathodes. This condition is not very objectionable in electrotyping, as slight roughness on the back of electrotype shells is not a serious defect. In electroplating, however, it is the layer of metal last deposited which determines the appearance of the coating. Therefore, it is not generally feasible to employ violent agitation in plating solutions. The

roughness can be overcome in part by the use of bags around the anodes, or by frequent or continuous filtration of the solutions. Continuous circulation and filtration produces moderate agitation.

There are various mechanical plating devices in which the cathodes are conveyed through the solution by means of a chain or a screw conveyor or upon arms from a central axis. In addition to providing a mild form of agitation, many such machines serve as labor-saving devices by automatically cleaning, pickling, plating, rinsing, and drying the work. The degree of agitation secured as a result of the movement of the cathodes is helpful in permitting the use of current densities slightly higher than normal but by no means equal to what might be secured by more rapid agitation were such feasible. There are great possibilities of increasing the current density by improved methods of agitation, especially for large-scale production of similar articles.

In *barrel plating*, which is used for small articles, such as nuts, bolts, screws, washers, etc., a high degree of agitation is secured, *e.g.*, by the rotation of the work in a cylinder immersed in the plating solution. One reason that this agitation does not cause roughness from suspended particles is that during the operation the articles are subjected to a slight continuous burnishing action, which counteracts any tendency to roughness.

The simplest form of plating barrel consists of an open cylindrical tank which rotates upon an axis inclined at about 45 deg. The anodes are hung directly in the solution. The articles are placed directly in the barrel, making contact with the cathode by suitable bars attached to the barrel. By the rotation of the barrel the objects tumble over each other and thus continually expose a fresh surface for plating. This type of barrel has the advantage of simplicity of construction, but the disadvantage that, in order to remove the work from the barrel, the solution must be emptied into some other receptacle. It is not, therefore, adapted to work upon a very large scale. Another disadvantage is that in such a barrel the anode area is usually very limited, and hence the anode efficiency may be low.

By far the greater number of plating barrels consist of a perforated cylinder mounted on a horizontal axis and connected to the cathode, within which cylinder the articles are placed. This cylinder is rotated in a tank containing the plating solution

and the anodes, which latter are sometimes curved so as to be approximately parallel to the circumference of the cylinder. The latter is in fact usually not a cylinder, but a hexagonal or octagonal prism, one of the long sides of which can be opened to introduce or remove the articles.

One of the most difficult problems in the construction of a plating barrel is the material for the perforated diaphragm. The simplest and cheapest material is wood, which is extensively used in the form of strips with holes as small as necessary to prevent the articles from passing through. In spite of the fact that wood is attacked by the solutions and is abraded by the rubbing of the metal articles, it was more generally used than any other substance. Celluloid, bakelite and rubber are now employed and their greater service makes up for increased cost. Wooden cylinders are sometimes provided with relatively large holes, and coarse cloth or canvas is stretched over the frame and supported by wooden strips.

Although the plating barrel is the most practicable way of plating small objects on a large scale, it is not electrically efficient. In those types using a diaphragm, the resistance is relatively high, but by using solutions of low resistivity, barrel plating can be done with 6 volts just as with the ordinary plating tank. The actual current density secured is difficult to measure, owing to the uncertainty as to the effective cathode area. At any given time only part of the objects are actually in the circuit, and of them only a small proportion of the surface is effective. Other conditions being equal, it is therefore desirable to use in a plating barrel a solution with high metal content, good conductivity, and good throwing power. The latter property is useful in permitting deposition on parts of the surface that are relatively inaccessible. Usually, barrel plating solutions have from one and one-half to twice the metal content of the regular solution.

4. CIRCULATION AND FILTRATION

It is necessary to filter plating solutions at intervals, and at the same time remove any sludge accumulated upon the bottom of the tanks. For large installations and conveyor systems continuous filtration is essential. In order to do this efficiently, some means of pumping the liquids is desirable. For nearly neutral solutions, bronze pumps may be used. For strongly

acid solutions, however, it is necessary to use hard rubber, lead, or some acid-resisting iron, *e.g.*, the high silicon irons, such as "Duriron," "Duralloy," "Tantiron," and "Corrosiron." Antimonial lead or lead alloyed with calcium or barium is also used for this purpose.

Owing to the practical difficulties in the operation of pumps with moving parts, there are certain advantages in the use of compressed air for pumping. This is accomplished by various devices, one of which, known as the "air-jet lift," may be used very conveniently for acid copper solutions, provided compressed air at about 5 lb./sq. in. is available. It may be constructed of brass or bronze for neutral solutions, but for strongly acid solutions lead is preferable. Solutions may also be conveyed by a steam injector pump, which, however, is less satisfactory because the steam heats and dilutes the solution. The air-jet lift type of pump is very compact, and occupies only a very small space, partly in the tank and partly outside. It is employed in a very compact pump and filter recently developed for continuous filtration of solutions. In certain cases, filter presses with bronze or wooden parts have been applied successfully to plating solutions. Such a press, together with a suitable motor and pump, can be made portable by mounting it on a truck. Centrifugal filters are also used but are expensive.

When a considerable number of tanks are used with the same solution and the same kind of work it is often an advantage to circulate and mix the contents so that there is only one solution to be analyzed and adjusted. In large copper refining plants this circulation is usually accomplished by having the tanks in cascade (*i.e.*, arranged on successive levels) or by allowing the solution to overflow from the tanks into a reservoir or sump, from which it is pumped to an elevated storage reservoir from which it flows back to the tanks. These methods are now being adapted to large electroplating and electrotyping plants. In such installations for nickel plating, care should be exercised to avoid aeration of the solutions, which may lead to pitting.

Filters for the nearly neutral solutions may consist of muslin, which should be previously thoroughly soaked and washed with soap and water to remove any sizing such as dextrin, which in even small amounts may act as a harmful addition agent. For acid copper solutions, wool cloth should be used, and this should be washed out when not in use, or at least the solution should

not be allowed to concentrate upon it by evaporation. For alkaline solutions, sand or asbestos filters may be used.

5. LOCATION OF TANKS

The tanks should always be raised from the floor by resting upon bricks, concrete, or wood impregnated with asphalt. This permits frequent cleaning of the floor, and also aids in the detection of leaks. The floor should, wherever possible, be made of concrete or of vitrified brick or tile with cement joints, laid with a slope of at least 1/8 in. to the foot toward a drain. A bituminous surface is especially advantageous where acid solutions are used. A false floor of wooden strips is usually placed where the workman walk. The actual position of the plating and cleaning tanks will depend upon the type of work and the procedure used, but it should at least be arranged with a view toward saving steps, *i.e.*, the work should progress through or around a room. Those tanks using the highest currents should, wherever possible, be located nearest to the generator. Large stoneware tanks should rest upon several inches of sand to reduce strains that may come from settling of the floors.

CHAPTER XIII

COPPER DEPOSITION

The order in which the deposition of specific metals is discussed is largely arbitrary. The arrangement here selected is based not so much upon the relative importance of the various metals in electrodeposition as upon the convenience of presentation. Copper deposition is treated first because in the sulphate solution we have a simple illustration of an acid bath, and in the cyanide solution a typical, although not so simple, illustration of an alkaline bath. The other elements, the deposition of which is industrially important, are considered in groups determined in part by their chemical and electrochemical similarities.

The two principal copper baths in commercial use are the acid sulphate and the alkaline cyanide solutions. The former has great advantages in simplicity and ease of operation and is therefore used almost universally for electroforming, as in electrotyping, the manufacture of tubes, floats, etc. It is used less extensively for plating because it is not applicable for the direct deposition of copper on iron, zinc, or other metals above copper in the electromotive series. If this is attempted, deposition of copper by immersion occurs, and a spongy, non-adherent coating is usually produced. Frequently an acid copper solution is used for plating antimonial lead articles, such as novelties, fixtures, etc., on which the copper serves as a base for ornamental finishes. Steel is often given a very light "wash" of copper by immersion in a solution containing about 15 g./l. (2 oz./gal.) of copper sulphate and 13 g./l. (1 fl. oz./gal.) of sulphuric acid, producing deposits which have a slight temporary protective action. The cyanide copper solution finds extensive application in plating iron. Deposits of copper from this solution usually serve only as a base for ornamental finishes or for subsequent plating with nickel or silver, or with copper from the acid solution. They do not of themselves furnish any appreciable protection against corrosion of the iron. C. J. Wernlund[1] has shown that under properly selected condi-

[1] *Metal Ind.*, vol. 20, p. 106, 1922.

tions it is possible to produce thick, hard deposits of copper from cyanide solutions.

One important use of cyanide copper solutions is for plating steel preparatory to case-hardening, in which process the copper serves to protect those parts which are not to be hardened. The thickness of copper required to protect the steel against case-hardening depends upon the temperature and period of treatment.[1] For most purposes a thickness of 0.013 mm. (0.0005 in.) of copper is sufficient. A simple test has been devised[2] to determine whether an adequate thickness has been applied. This consists in applying to the surface a drop of 1–1 nitric acid and noting the time required before the copper is dissolved and the steel is attacked. Deposits of the above specified thickness require 45 to 50 seconds in this test.

McCollough and Reiff[3] concluded that the protective value of the copper against case-hardening depends not so much upon the thickness of the copper as on its porosity. The structure of the base metal also influences the porosity. The latter can be readily determined by the ferricyanide test (p. 131). Practically however for a given base metal, the porosity under given conditions of deposition is determined largely by the thickness and by the structure of the deposits.

It was reported by J. Satka[4] that by dipping iron or steel into a solution made by dissolving 60 g./l. (8 oz./gal.) of arsenic trioxide (As_2O_3) in concentrated hydrochloric acid, the iron becomes coated with arsenic and can then be plated directly in the acid copper bath. This process has been quite extensively used in the last few years. This subject was subsequently studied by O. P. Watts,[5] whose results show that in the above solution the potential of arsenic is between that of iron and copper; therefore, the arsenic is deposited in a more adherent form by immersion of the steel than the copper would be in the sulphate solution.

1. ACID COPPER SULPHATE BATHS

(a) Constituents.—The acid copper bath is probably the oldest, simplest, and (if we include electrorefining) the most

[1] Vanick, J. S., and Herschman, H. K. *Trans. Am. Soc. Steel Treating*, vol. 4, p. 305, 1923.

[2] Maeder, R. E., *Month. Rev., Am. Electroplaters' Soc.* vol. 9, no. 11, p. 5, 1922.

[3] *J. Ind. Eng. Chem.*, vol. 16, p. 611, 1924.

[4] *Monthly Rev., Am. Electroplaters' Soc.*, vol. 5, no. 8, p. 5, 1918.

[5] *Trans. Am. Electrochem. Soc.*, vol. 35, p. 265, 1919.

used electrodepositing solution. The only two essential constituents, in addition to water, are copper sulphate ($CuSO_4$) and sulphuric acid (H_2SO_4). The former is always obtained commercially as the crystallized salt ($CuSO_4.5H_2O$), commonly known as "blue vitriol," which contains when pure, 25.4 per cent of copper. It is usually produced as a by-product of copper refining, and therefore contains some impurities, such as iron, arsenic, and zinc. Fortunately, however, the amounts of these impurities are usually less in the salts than in the solution from which they were crystallized. As in the acid copper refining bath, care must be used to prevent even minute amounts of arsenic or other impurities from contaminating the refined copper, it is reasonable to assume that the salt crystallized from such a solution will be pure enough to be used in electrotyping or electroplating baths. It is doubtful whether any specification is necessary to secure this salt of the required purity. The presence in it of a small amount of free sulphuric acid is not objectionable (except as it may cause contamination by attacking the paper, cloth, or wood in which the salt is packed). A content of iron up to 0.1 per cent is apparently harmless. Arsenic is detrimental only if present in appreciable amounts. These facts emphasize the importance of confining specifications for plating salts or chemicals to the limitation of actually harmful constituents. Of course on general principles it would be desirable to use in all the solutions only salts of high purity, but the cost of securing, and especially of assuring, such a high degree of purity is prohibitive. Thus in one electrotyping plant tests for several years showed that the commercial copper sulphate secured without specifications contained in every case less than 0.03 per cent Fe. When, however, a specification was inserted that the salt should contain not over 0.05 per cent Fe, it was impossible to secure any bids, probably because the dealers were unable to guarantee the purity and did not wish to have analyses made.

The whole subject of specifications for plating chemicals is greatly in need of study, which can best be conducted with the cooperation of the electroplaters and chemical manufacturers. The preparation of mutually satisfactory specifications involves extended investigation not only of the effects of various impurities in specific baths, but also the sources and methods of manufacturing the salts on a commercial scale. Where some impurity

is found to be especially harmful it may be possible to exclude or eliminate it with very little extra cost.

Commercial sulphuric acid is generally of sufficient purity for the acid copper bath. It may contain small amounts of arsenic, iron, nitrates and chlorides, and organic matter. Of these the latter is the most likely to be detrimental, as it may act as a harmful organic addition agent, although so far as known no such difficulty has been reported. As in practice, frequent additions of sulphuric acid are usually required, and very little copper sulphate is added, it is more important to employ pure sulphuric acid than pure copper sulphate, and in some cases the use of C.P. acid may be justified.

(b) **Composition of Baths.**—The proportion of the two constituents of the acid copper bath may vary over wide limits and still permit satisfactory copper deposits to be secured. The best deposits are, however, obtained only within more restricted limits. There is an obvious advantage of using solutions with a high content of copper sulphate. This is readily accomplished, as this salt has a solubility in water at 25°C. (77°F.) of 352 g./l. (47 oz./gal.), and appreciably greater solubility at higher temperatures. However, the addition of sul-

Solubility of Copper Sulphate in the Presence of Sulphuric Acid at 25°C. (77°F.)[1]

Sulphuric acid present			Solubility of copper sulphate ($CuSO_4.5H_2O$)		
N	g./l.	oz./gal.	*N*	g./l.	oz./gal.
0	....	...	2.82	352	47.2
0.5	24.5	3.3	2.61	326	43.7
1.0	49.0	6.6	2.42	304	40.8
1.5	73.5	9.9	2.28	285	38.2
2.0	98.1	13.1	2.14	267	35.8
2.5	122.6	16.4	2.00	250	33.5
3.0	147.1	19.7	1.84	230	30.8
3.5	171.6	23.0	1.70	212	28.4

[1] Derived from paper by Goodwin H. M. and Horsch, W. G., *Chem. Met. Eng.*, vol. 21, p. 181, 1919.

phuric acid decreases this solubility very materially, as shown in the above table. Thus 49 g./l. (6.6 oz./gal.) of sulphuric acid reduces the solubility of the copper sulphate to 304 g./l. (40.8 oz./gal.). It is obvious that for any desired content of sulphuric acid it is necessary to keep the concentration of copper sulphate appreciably below its corresponding solubility in order to avoid crystallization of the salt upon the anodes. For practical purposes we may consider from 150 to 240 g./l. (20 to 32 oz./gal.) as the limits of favorable concentration of crystallized copper sulphate.

The presence of sulphuric acid in copper baths is advantageous in several respects; in fact, it is a splendid example of how a single substance may be used to serve several useful purposes. If a neutral solution of copper sulphate is electrolyzed at fairly high current densities, especially without agitation, a spongy deposit contaminated with cuprous oxide (Cu_2O) will be produced, and the anodes may become coated with the same substance. This is because there is a tendency in the electrolysis of copper sulphate solutions to reduce part of the copper in the solution to the cuprous state (*i.e.*, having a valence of +I instead of +II, as in the cupric salts). The cuprous sulphate tends to hydrolyze (*cf.* page 32), and unless appreciable free sulphuric acid is present, a precipitate is formed. The sulphuric acid serves the purpose of preventing the formation of basic salts.

Resistivity of Copper Sulphate-Sulphuric Acid Solutions[1] at 25°C. (77°F.) in Ohm-cm.

H_2SO_4 g./l. / $CuSO_4.5H_2O$ g./l.	0	50	100	150	200
0	..	4.8	2.44	1.77	1.46
50	65	4.9	2.58	1.88	1.55
100	45	5.1	2.86	2.00	1.67
150	29	5.3	3.04	2.18	1.79
200	24	5.5	3.14	2.31	

[1] Calculated from Richardson and Taylor, *Trans. Am. Electrochem. Soc.*, vol. 20, p. 179, 1911.

Another important function of sulphuric acid is to decrease the resistivity of the bath. Copper sulphate solutions, like

those of other heavy metal sulphates, have a relatively high resistivity. By the addition of sulphuric acid the resistivity of the solution can be greatly reduced, as shown in the above table. The greater conductivity of the solutions containing sulphuric acid is due principally to the presence in them of a large number of hydrogen ions, formed by dissociation of the sulphuric acid. This is obvious from the table, in which it may be seen that in all solutions containing 50 g./l. or more of sulphuric acid the presence of the copper sulphate actually increases the resistivity of the solutions. The fact that copper baths with high concentrations of sulphuric acid can be used makes them by far the best conducting of the ordinary depositing solutions except chromic acid baths. As explained on page 95, this increase in conductivity not only reduces the cost of power but also decreases the tendency toward the formation of rough and treed deposits at relatively high current densities. It is possible to obtain good deposits of copper from strongly acid solutions, because in the electromotive series (Table 10) the copper is appreciably below hydrogen, *i.e.*, it is much easier to deposit copper than hydrogen. Therefore, even with high concentrations of sulphuric acid, and hence of hydrogen ions, the copper is deposited in preference to the hydrogen, and the metal cathode efficiency is high. The limiting concentration of sulphuric acid is reached when the solubility of the copper sulphate is so reduced that (for a given current density) the copper content of the solution at the cathode is not replenished rapidly enough to prevent deposition of hydrogen. As agitation is equivalent to an increase in metal concentration (page 90), it is possible to use in agitated copper solutions a higher content of acid and lower content of copper sulphate than is possible in still solutions. For practical purposes, with good air agitation and current densities up to 10 amp./dm.^{2} (93 amp./sq. ft.) at ordinary temperature, or up to 20 amp./dm.^{2} (185 amp./sq. ft.) at 45°C. (113°F.), the best concentration of sulphuric acid is about 75 g./l. (10 oz./gal.) *i.e.* 1.5 *N*, and of copper sulphate is about 240 g./l. (32 oz./gal.), *i.e.* about 2 *N*.

A still further beneficial effect of the sulphuric acid is its influence in decreasing the copper ion concentration (page 96). Thus in a normal solution of copper sulphate the addition of normal sulphuric acid reduces the copper ion concentration (as calculated from the single potential of copper) from about 0.11 *N* to 0.06 *N*. While this change is far less than that pro-

duced by the formation of a complex ion, it is sufficient to have some favorable effect in reducing the size of the copper crystals.

(c) **Reactions during Electrolysis.**—At first glance, the reactions which occur in the electrolysis of an acid copper sulphate solution appear very simple. If we consider the copper salt as dissociated into Cu^{++} and SO_4^{--}, the cathode reaction consists in the discharge of the cupric ions to form metallic copper; and the anode reaction in the combination of the sulphate ions with the copper of the anode to form copper sulphate. If these, and only these, reactions occurred, the bath would remain constant in composition, and there would be no need for any additions except to replace mechanical losses. Actually, however, it is found that in the electrolysis of such a bath, especially when agitated with air, there is a gradual decrease in the acidity and a corresponding increase in copper sulphate concentration. This is equivalent to stating that there is a greater amount of metal dissolved from the anode than is deposited upon the cathode, or that the anode efficiency is higher than the cathode efficiency.

As in this bath the cathode efficiency (calculated as cupric copper) over a considerable range of conditions is very close to 100 per cent, it follows that the anode efficiency must be over 100 per cent if the copper content increases. This apparent anomaly is explained by the fact that copper can exist in ions corresponding to two states of oxidation, cuprous (Cu^{+}), having a valence of one, and cupric (Cu^{++}), with a valence of two. Ordinarily in the copper sulphate bath we assume that the copper is in the cupric state. As a matter of fact, however, there is always in such solutions, when in contact with copper, a small amount of copper in the cuprous state, and there is a tendency for copper to pass into solution from the anode to form cuprous ions (Cu^{+}). As the electrochemical equivalent of cuprous copper is twice as great as that of cupric copper, it follows that just to the extent that cuprous ions are formed, more copper will pass into solution from the anode than if only cupric ions were formed. If we had in a solution a constant proportion of cuprous and cupric ions, and the reaction at the cathode was exactly the reverse of that at the anode, there would be no change in the copper content of the solution.

There is, however, a tendency in such solutions for the cuprous ions to be oxidized to cupric ions. This oxidation may result directly from the oxygen dissolved in the solution. If, as is

usual in electrotyping baths, the solution is agitated with air, it will always be saturated with oxygen, and hence under such conditions the cuprous ions will be readily oxidized, and additional cuprous ions will be formed at the anode. The net result is an increase in the content of copper sulphate and a decrease in that of free sulphuric acid:

$$\underset{\text{cuprous sulphate}}{Cu_2SO_4} + H_2SO_4 + O = \underset{\text{cupric sulphate}}{2CuSO_4} + H_2O$$

It is also possible for the cuprous ions to be oxidized to cupric ions by a reaction in which part of the copper is reduced to metallic copper, which may be represented thus:

$$Cu_2SO_4 = CuSO_4 + Cu$$

or

$$2Cu^{+} = Cu^{++} + Cu$$

This reaction results in the formation of very finely divided copper, which may separate on the anodes or fall to the bottom of the tank as sludge. The exact reactions that occur at the anode and cathode under any given conditions may be more complicated. It has been suggested[1] that copper always dissolves and deposits *electrochemically* in the cuprous state, and that its oxidation to or reduction from the cupric state is due either to secondary electrochemical processes, or to a direct chemical action. This theory has the advantage of simplicity, and of applicability to other metals which may exist in solution with more than one valence.

From a practical operating standpoint the increase in copper content and decrease in acidity, caused by the formation and oxidation of cuprous ions, is seriously objectionable, as it is difficult to dispose of the excess copper sulphate thus formed. In electrotyping, if the so-called oxidizing process is used (page 167), the copper sulphate solution removed periodically to reduce the copper content can be used after dilution. The conditions of operation that are otherwise favorable, *viz.*, high acidity, air agitation, and the use of large anode areas (and consequent low anode current density) are the very conditions which favor the formation and oxidation of cuprous ions. If the acidity is decreased or the anode area is reduced, the resistance of the bath

[1] Briggs, J. R., *Trans. Am. Electrochem. Soc.*, vol. 40, p. 231, 1921.

is correspondingly increased, and there may be difficulty in obtaining with the available e.m.f., the desired cathode current density. It is possible to remove the excess of copper sulphate and at the same time regenerate the sulphuric acid, by the introduction, either regularly or at intervals, of a certain proportion of lead anodes. Their use, however, has the disadvantage that, owing to the counter e.m.f. set up by the copper-lead peroxide cell thus produced, the current density opposite the lead anodes is much less than that opposite the copper anodes. A more serious difficulty, however, is that at the lead anodes oxygen is evolved, which carries into the atmosphere a fine spray of the solution, which is very penetrating and irritating to the throat and lungs. It is not practicable in a electrotyping plant to keep a film of oil on the surface, as is usually done in electrolytic copper refineries when lead anodes are used. Unless, therefore, the plant is provided with exceptionally good ventilation, it is necessary to carry out the electrolysis with lead anodes as a separate operation. Where waste steam is available, it may be found more practical to evaporate portions of the solution at intervals in lead-lined tanks, and to crystallize out some of the excess of copper sulphate. At best any one of these operations is troublesome for a small plant, and hence we find that most of the copper sulphate removed when the solutions are "cut down" is thrown away. In spite of this fact, it was found several years ago that many electrotyping plants were adding large amounts of copper sulphate to their baths! If simple tests are made (even with a hydrometer), it may be shown that under usual conditions no copper sulphate need be added to such a bath, as the mechanical losses are more than balanced by the excess formation of sulphate. By the addition of sulphuric acid as required, the desired copper content will always be maintained and may be exceeded. Such a bath, therefore, in effect manufactures copper sulphate from copper and sulphuric acid.

(d) **Copper Anodes.**—As practically all the copper upon the market has a very high purity, there is not much chance of contamination of the baths from impurities in the anodes. Copper is secured from two principal *sources:* from native copper found chiefly in the vicinity of Lake Superior and known as "lake copper," which contains almost no metallic impurities and requires very little refining; and from sulphide or oxidized

ores which may contain many other metals, which latter are removed by various smelting and refining operations. As the last operation in this purification is electrolytic refining, the product is usually known as "electrolytic copper." At the present time copper from these two sources is equally pure and there is no preference so far as use in anodes is concerned.

Copper from either source may be purchased in the *form* of electrolytic, cast, or rolled anodes. The electrolytic anodes are those deposited either in refining or in a separate operation and not subjected to further treatment. Cast anodes are made by melting and casting the lake or electrolytic copper; and the rolled anodes are formed by reheating and rolling cast copper bars. Extruded copper, formed by forcing the hot metal through a die, is very similar to rolled copper. Assuming equal freedom from metallic impurities, any differences in the behavior of these anodes must be due to differences in their physical structures, which are likely to manifest themselves in irregularities of anode corrosion or in the formation of unusual amounts of sludge, which in almost every case consists of finely divided copper.

Rolled or extruded anodes are most satisfactory, both for cyanide and acid copper solutions, and are extensively used. In most cases disc anodes are now made of rolled copper. It is generally agreed that the cast anodes are the least satisfactory in acid copper baths. This is probably because (1) in casting there is a tendency for the formation of cuprous oxide, (2) the crystals in cast copper are relatively large, and (3) there is an opportunity, especially with slow cooling, for the cuprous oxide and the impurities (which may be present in very minute amounts) to segregate between the crystals. In general, such impurities increase the solution pressure of the copper, and hence there is a tendency for the copper to dissolve around the grains, allowing the latter to fall out as a sludge, which may cause rough deposits. If conditions are employed which will produce a dense, fine-grained casting, it is probable that satisfactory cast anodes can be made.

In the process of reheating and rolling, a finer crystal structure is produced and the mechanical working tends to produce copper with a uniform solution pressure. In consequence, rolled anodes are almost universally used in acid copper baths.

Electrolytically deposited copper is apparently intermediate in behavior between the rolled and cast copper. Especially when deposited in refining baths at relatively low current densities

without decided agitation, the crystals are fairly large and there is a tendency toward striations and rough projections. At present however, selected cathodes are being cut to the desired sizes and used extensively for copper electrotyping solutions. If there was a regular demand for electrolytic copper in a few simple sizes, it would probably be possible to purchase it at lower prices than those of rolled or cast anodes.

(e) Operating Conditions.—The effects of various operating conditions upon the structure and properties of deposits from the acid copper solution have been extensively studied, and serve as excellent illustrations of the principles involved. Since, as previously stated, this solution is largely used in electrotyping, the hardness and tensile strength of the deposits are of special interest. In the absence of adequate methods of directly measuring the hardness or resistance to abrasion, the ultimate tensile strength may be taken as an index of durability, *e.g.*, on a printing plate.

In general, the effects observed are in accordance with the principles discussed in Chap. VII. Provided sufficient copper sulphate is present to secure a high cathode efficiency at the current density used, its concentration has little effect upon the deposits. An increase in the sulphuric acid content, up to that concentration which causes low efficiency, produces finer-grained deposits, which have high tensile strength. An elevation in temperature always produces coarser and softer deposits. This effect of even a small change in temperature may be very great; thus at a current density of 5 amp./dm.^{2} (47 amp. /sq. ft.), increasing the temperature of deposition from 25 to 40°C. (77 to 104°F.), decreased the tensile strength from 2,800 to 1,400 kg./cm.^{2} (40,000 to 20,000 lb./sq. in.). As the current density is increased it tends to increase the tensile strength, and its effect is more pronounced than that of the temperature. Consequently, at higher current densities, *e.g.*, 8 to 10 amp./dm.^{2} (74 to 93 amp./sq. ft.), an increase in temperature does not produce as much harmful effect as at lower current densities. The influence of agitation in permitting higher current densities to be used is very marked in acid copper solutions.

Most attention has been paid to the effect of the solution composition upon the character of the cathode deposit. Recent unpublished experiments by R. O. Hull at the Bureau of Standards show that when high current densities are employed, the

anode polarization may be so high that excessive voltages are required. This anode polarization can be decreased by increasing the temperature, agitation and content of sulphuric acid, and by decreasing the content of copper sulphate.

Although the effects of a great many addition agents in copper solutions have been studied, very few have found commercial application, and these with only moderate success. About 2 oz./gal. (15 g./l.) of aluminum sulphate is beneficial in baths used for plating and ornamental work. Glue and casein have been used frequently, but owing to the impossibility of controlling their concentration by chemical analysis, difficulties are sometimes encountered, such as the production of brittle copper. Dextrose is often added either in the form of corn sugar or syrup, or as molasses, the cane sugar of which is subsequently inverted by the acid present to form reducing sugars. Corn syrup also contains considerable amounts of dextrin, a colloidal substance. Sometimes erratic results, such as the production of very dark deposits, are obtained when sugars are used.

In the study of R. O. Hull the use of phenol as an addition agent was investigated. It was found to yield harder and smoother deposits than can be obtained with only copper sulphate and sulphuric acid. The phenol is best added as phenolsulphonic acid, which is made by heating equal volumes of phenol and concentrated sulphuric acid to about 100°C. (212°F.) for about one hour. One gram per liter (0.13 oz./gal.) of phenol is used in the copper bath. Its action may be partly due to substances formed from it in the bath on extended operation. Its presence permits somewhat higher current densities to be used.

(f) Suggested Formulas.

1. Copper Electrotyping

	Approx. *N.*	g./l.	oz./gal.
Copper sulphate ($CuSO_4.5H_2O$)	2.0	250	33.0
Sulphuric acid (H_2SO_4).....	1.5	75	10.0

Temperature 25 to 35°C. (77° to 95°F.)

Current density (in well agitated solutions) 8 to 16 amp./dm.^{2} (75 to 150 amp./sq. ft.).

2. Copper Plating

Copper sulphate ($CuSO_4.5H_2O$.)	1.6	200	27.0
Sulphuric acid (H_2SO_4).....	1.0	50	6.5

Temperature 25° to 50°C. (77° to 122°F.)

Current density 2 to 4 amp./dm.^{2} (19 to 37 amp./sq. ft.).

(g) **Analysis of Solutions.**—The analysis of acid copper solutions may be carried out with very simple apparatus. The free *sulphuric acid* can be titrated directly, using methyl orange as the indicator. The color change at the end of the titration is from a purple to a nearly colorless or faint green solution. A 10-c.c. sample of the solution is measured into a small flask, diluted to about 25 c.c., and a few drops of methyl orange (1 to 1,000 aqueous solution) are added. A standard solution of sodium hydroxide is then run in from a burette until, after shaking, the purple color just disappears. If, *e.g.*, the alkali is normal, 1 c.c. = 0.049 g. of sulphuric acid. The acidity is then easily calculated as follows:

$$\text{No. of c.c. of alkali} \times 0.049 \times \frac{1{,}000}{10} = \text{g./l. } H_2SO_4.$$

Thus if 15.4 c.c. of alkali are used, $15.4 \times 0.049 \times 100 = 75.5$ g./l., or for practical purposes, 75 g./l. $75 \times 0.134 = 10$ oz./gal.

The *copper* content of the solution can be most readily determined electrolytically (page 39). A 10-c.c. sample is diluted to, *e.g.*, 100 c.c, and a few drops of nitric acid are added. The electrolysis is then conducted either with platinum electrodes, or with a copper cathode and a platinum or lead anode. The cathode with the deposited copper is weighed after drying in the usual way. If it is desired to calculate the content of copper sulphate, this can be done as follows:

If 10 c.c. of the solution yield 0.513 g. of copper, the solution contains $100 \times 0.513 = 51.3$ g./l. of copper. As copper sulphate contains 25.4 per cent of copper, this is equivalent to $\frac{100}{25.4} \times 51.3 = 202$ g./l. (27 oz./gal.) of copper sulphate.

The copper may also be determined by titration with sodium thiosulphate ($Na_2S_2O_3$). In this method the sample, *e.g.*, 5 c.c., is diluted to 50 c.c. with water, ammonium hydroxide is added until a deep blue color is just produced, and then acetic acid is added in excess, *i.e.*, till the deep blue color disappears, and a light blue or greenish solution is produced. The solution is allowed to cool, after which 2 g. of potassium iodide (KI), or 10 c.c. of a 20 per cent solution of KI, are added. The solution is then titrated with a standard solution of sodium thiosulphate ($Na_2S_2O_3$) until the brownish color almost disappears. A few drops of a starch solution (made by pouring a paste of 1 g. of

starch into 100 c.c. of boiling water) are then added, and the titration is continued till the blue color just disappears.

A 0.1 *N* sodium thiosulphate solution may be made by dissolving 25 g. of the crystallized salt ($Na_2S_2O_3.5H_2O$) and diluting to 1 l. It may be standardized by means of metallic copper, which is dissolved in nitric acid, evaporated nearly to dryness, taken up in water, and then treated with ammonia, acetic acid, and potassium iodide as above described. The reactions involved are as follows: In the solution, which has been acidified with acetic acid, we may assume that the copper is present as cupric acetate, $Cu(C_2H_3O_2)_2$. When potassium iodide is added to this solution, a white precipitate of cuprous iodide (Cu_2I_2) and a brown precipitate of iodine (I_2) are formed.

$$2Cu(C_2H_3O_2)_2 + 4KI = Cu_2I_2 + I_2 + 4KC_2H_3O_2$$

Upon titration with sodium thiosulphate, the iodine is dissolved according to the following equation:

$$2Na_2S_2O_3 + I_2 = Na_2S_4O_6 + 2NaI$$

The starch (which produces a blue color with free iodine) serves to indicate, by the disappearance of the blue color, when the iodine is entirely combined.

Example.—Suppose 0.252 g. of pure copper was dissolved and upon titration required 41 c.c. of $Na_2S_2O_3$. Then 1 c.c. of the latter solution must be equal to $\frac{0.252}{41} = 0.00615$ g. Cu. If 5 c.c. of the copper plating solution required 47 c.c. of the $Na_2S_2O_3$ solution, the copper content must be:

$$47 \times 0.00615 \times \frac{1{,}000}{5} = 57.7 \text{ g./l. (7.7 oz./gal.) Cu}$$

or

$$57.7 \times \frac{250}{63.6} = 227 \text{ g./l. (30.5 oz./gal.) } CuSO_4.5H_2O$$

For solutions which do not contain appreciable amounts of substances other than copper sulphate and sulphuric acid, it is possible to determine the content of copper sulphate from the specific gravity and acidity. This is an illustration of the value of density readings when accompanied by other data. The density alone (as determined, *e.g.*, by a hydrometer) is not a measure of the composition when, as in this case, two constituents are present in the solution. Tables have been prepared[1]

[1] Holler, H. D., and Peffer, E. L., Bureau of Standards, *Scientific Paper 275.*

of the density of copper sulphate-sulphuric acid solutions of varying composition. It was found that the specific gravity of solutions containing a given total concentration of copper sulphate plus sulphuric acid is independent of their proportions. Thus, *e.g.*, a solution containing 150 g./l. of copper sulphate and 100 g./l. of sulphuric acid has the same specific gravity as one with 200 g./l. of copper sulphate and 50 g./l. of sulphuric acid. This agreement, which appears to be only a mathematical coincidence, makes it very easy to prepare a table showing the total concentration in any solution of a given specific gravity. Such a table (Table 13) is given in the Appendix.

Suppose now it is found that a copper solution has a specific gravity of 1.18 (22.1°Bé.), and that it contains (as determined by titration) 75 g./l. (10 oz./gal.) of sulphuric acid. According to Table 12 this specific gravity corresponds to a total concentration of 303 g./l. (40.6 oz./gal.); therefore the content of copper sulphate is 303 − 75 = 228 g./l.; or 40.6 − 10 = 30.6 oz./gal. By the use of this table it is possible to control the composition of the copper solutions without any actual determination of copper, except perhaps occasionally to serve as a check upon the possibility of marked contamination by other substances.

If, as is usually the case in agitated acid copper solutions, the periodic analysis shows an increase above the desired copper sulphate content, the proportion of the solution to be removed is easily calculated.

Example.—Suppose that in the above case a concentration of 200 g./l. of copper sulphate is desired, *i.e.*, the solution has an excess of 28 g./l. Then it is necessary to remove $\frac{28}{228}$ = 12 per cent, or 1/8 of the solution, *e.g.*, 75 l., or 20 gal., if the tank contains 600 l., or 160 gal. As in this operation 12 per cent of the sulphuric acid is also removed, the remaining acid is equivalent to only 88 per cent × 75 g./l. = 66 g./l. If then it is desired to have 80 g./l. of acid, it is necessary to add 14 g./l. of acid, *i.e.*, 14 × 600 = 8,400 g., or 18.5 lb., for the bath. As commercial concentrated sulphuric acid contains about 95 per cent H_2SO_4, about 5 per cent more of the commercial acid than that just calculated must be used.

2. CYANIDE COPPER SOLUTION

The essential constituent of the alkaline copper solutions which are now used is sodium cuprocyanide, the formula of which is probably 2NaCN.CuCN, or $Na_2Cu(CN)_3$. This compound con-

tains copper in the cuprous state (Cu^{+I}). If directly or indirectly the cyanide solution is prepared from copper sulphate or other cupric salts, the copper must be reduced to the cuprous state.

(a) **Constituents.**—The simplest method of preparing such solutions is by dissolving cuprous cyanide (CuCN) in sodium cyanide (NaCN), both of which materials are commercially available. Sodium cyanide is now used almost exclusively in place of the potassium cyanide which was formerly employed. This change came about principally because of the scarcity of potassium salts during the war. It has been found that in most plating solutions the two compounds are practically interchangeable, although for silver plating the potassium salt is usually preferred. Some of the difficulties encountered in the substitution of sodium for potassium cyanide were due to failure to take into account their equivalent weights. As the molecular weight of potassium cyanide is 65 and that of sodium cyanide is 49, 49 lb. of sodium cyanide contain the same amount of cyanogen (CN) as 65 lb. of potassium cyanide, and therefore a correspondingly less amount of the sodium compound is required to produce a chemically similar solution. When the sodium cyanide replaced the potassium salt, it was at first evaluated in terms of its potassium cyanide equivalent, which led to such anomalous statements as "sodium cyanide, 130 per cent," indicating that 1 lb. of the sodium cyanide was equivalent to 1.3 lb. of pure potassium cyanide. It is much less confusing to express the strength directly in terms of sodium cyanide, or of the cyanogen content.

Sodium cyanide and *potassium cyanide* are white solids, usually sold in the form of broken pieces, or of specially shaped lumps. The latter are useful in obviating the necessity of breaking up the solid or of handling powdered material. Owing to the fact that the cyanide is extremely poisonous, every precaution must be used against getting it into the system. Still more poisonous is the hydrocyanic acid (HCN), which is formed by the action of any (even very weak) acids or acid salts upon the cyanide. *No acid should, therefore, be allowed to come in contact with cyanide or solutions containing it.* If for special reasons (*e.g.*, to recover silver residues) it is necessary to add acid to a cyanide solution, the operation should be carried out where there is very effective ventilation, or preferably out of doors. To avoid this danger it is better to precipitate the silver with powdered zinc.

Sodium cyanide as purchased is usually designated as 95 to 98 per cent, and may safely be assumed to be within those limits, while potassium cyanide is usually only 92 to 94 per cent pure. If the container is frequently opened, some of the cyanide may be converted to carbonate by the action of carbon dioxide from the air. The principal impurities likely to be present are water and sodium carbonate, and small amounts of sodium sulphate or chloride. It may also contain thiocyanate (sulphocyanate, NaCNS), or complex cyanogen compounds. In general the small amounts of impurities present are very unlikely to prove injurious in plating baths. A specification of the cyanide content is therefore usually sufficient. Impure cyanide containing large amounts of chlorides or other impurities is not suitable for use in plating solutions, but may be applicable in cleaning baths.

Pure *copper cyanide* (CuCN) is a white powder, though the commercial product is yellowish in color. It is usually made by precipitating a *reduced* copper sulphate solution with sodium cyanide, and filtering and drying the precipitate. When pure it contains 71 per cent of copper and 29 per cent of cyanogen; but the commercial form contains only about 70 per cent of copper, and has as impurities small amounts of water and of carbonates and sulphates of sodium or copper. If not present in excessive amounts, these substances are not likely to prove harmful. If the salt contains much basic cupric carbonate or sulphate, additional cyanide will be required to dissolve it, owing to the necessity of reducing it to the cuprous condition. Its purity would best be specified in terms of the copper and cyanogen content. The former can be readily determined, but unfortunately the latter is a difficult estimation.

It is also possible to prepare cyanide copper solutions by dissolving basic copper carbonate in sodium cyanide. The *basic copper carbonate* may be considered as a mixture of cupric hydroxide, $Cu(OH)_2$, and cupric carbonate ($CuCO_3$), and may be represented as $Cu(OH)_2.CuCO_3$, which contains about 58 per cent of copper. As it is produced by precipitating a copper sulphate solution with sodium carbonate, it usually contains some basic cupric sulphate, and the copper content is only about 54 per cent. When basic cupric carbonate is dissolved in sodium cyanide, the copper is reduced and one-third of the cyanogen is evolved and lost. Great care should be used to avoid inhaling cyanogen (CN or C_2N_2), which is nearly as poisonous as hydro-

cyanic acid (HCN). The reaction may be shown for simplicity in separate equations.

$$CuCO_3 + 4NaCN = Na_2Cu(CN)_3 + Na_2CO_3 + CN$$
$$Cu(OH)_2 + 4NaCN = Na_2Cu(CN)_3 + {}_2NaOH + CN$$

This reaction is objectionable because of the waste of cyanide thereby involved. This can be prevented provided the copper is reduced by a cheaper reducing agent than sodium cyanide. Thus by adding sodium sulphite (Na_2SO_3) in the amount necessary to reduce the cupric copper, loss of cyanogen is avoided.

$$2CuCO_3 + Na_2SO_3 + H_2O + 6NaCN = 2Na_2Cu(CN)_3 + Na_2CO_3 + Na_2SO_4 + H_2CO_3$$
$$2Cu(OH)_2 + Na_2SO_3 + 6NaCN = 2Na_2Cu(CN)_3 + 2NaOH + Na_2SO_4 + H_2O$$

When this method is used, sodium sulphite (Na_2SO_3), and not bisulphite ($NaHSO_3$), should be employed, or else an equivalent amount of alkali, *e.g.*, NaOH, should be mixed with the bisulphite. With the latter compound, especially if an excess is used, there is grave danger of hydrocyanic acid being evolved, unless an excess of alkali is also present.

In preparing baths from copper carbonate, the temperature should not be allowed to exceed 120°F., as then some of the copper carbonate may be converted into the black oxide (CuO) which is very difficult to dissolve.

(b) **Composition of Baths.**—It will be observed that solutions produced by the solution of cupric carbonate contain, in addition to the principal compound, $Na_2Cu(CN)_3$, appreciable amounts of sodium carbonate, hydroxide, and possibly of sulphate. One of the advantages suggested for the use of metal cyanides, such as copper cyanide, is that they produce in the solution only the desired constituent, $Na_2Cu(CN)_3$, without any of the inert salts such as carbonates. This advantage is based upon the assumption that in plating solutions the latter compounds are unnecessary or even harmful. While very few definite experiments have been published upon the effect of such substances in the solutions, the results of practical experience indicate that up to certain amounts the alkaline carbonates are beneficial. (Large concentrations of carbonate are however detrimental.) In consequence, it is customary to add sodium carbonate to the solutions made from copper cyanide. It therefore appears that

in the preparation of solutions the use of copper cyanide is of advantage principally because it prevents loss of cyanogen and thus reduces the amount of sodium cyanide required. During operation of such solutions, however, especially when heated, the cyanide is decomposed and oxidized with the formation of sodium carbonate. The reactions which result in the formation of sodium carbonate may be represented thus:

$$2NaCN + 2H_2O + 2NaOH + O_2 = 2Na_2CO_3 + 2NH_3$$

The ammonia is evolved from the solutions, especially if they are heated or agitated. If there is no excess of alkali the carbonic acid formed may decompose the cyanide, liberating hydrocyanic acid. Even the carbon dioxide of the air may act upon the solutions, thus:

$$2NaCN + H_2O + CO_2 = Na_2CO_3 + 2HCN$$

Sodium cyanide may also be decomposed by a special form of hydrolysis, by which organic cyanides are changed to organic acids, such as formic acid (HCOOH). This can be illustrated by the reaction:

$$HCN + 2H_2O = HCOOH + NH_3$$

This reaction is especially likely to occur in weakly acid solutions, but even in alkaline solutions some formate (salt of formic acid) may be produced. In consequence of such changes, the cyanide content of the solutions decreases and that of carbonate increases, and if the metal content is maintained by addition of copper carbonate, the carbonate content of the solution is still further increased. The copper cyanide is therefore very useful for maintaining solutions, even those which may have been prepared from the metal carbonates.

Among the other substances which are often added to cyanide copper solutions is *sodium thiosulphate* ($Na_2S_2O_3$), usually called sodium hyposulphite or "hypo." Small amounts of this material are very useful in producing bright copper deposits, but an excess should be carefully avoided. (It has been observed that when deposits produced from solutions containing too much thiosulphate are subsequently "oxidized" with a sulphide, the resultant copper sulphide coatings are likely to be brittle.)

It seems probable that the effect of "hypo" is due to its reducing properties and to the fact that it is not so readily decomposed

as is sodium sulphite. When it is oxidized, the first products are the salts of so-called "polythionic" acids, *e.g.*, sodium dithionate ($Na_2S_2O_6$), which in turn may be slowly oxidized. There is need for a study of the exact reactions occurring in such baths. Small amounts of lead compounds, such as lead acetate, $Pb(C_2H_3O_2)_2$, or of lead carbonate dissolved in sodium hydroxide, are sometimes added as brighteners. In the alkaline solution the lead must be present in the form of either sodium plumbate (Na_2PbO_2) or sodium lead cyanide, $Na_2Pb(CN)_4$. No explanation for their effect has been suggested and it is not known whether any lead is deposited with the copper. The fact that such deposits do not acquire the normal black color when treated with a sulphide, at least indicates an appreciable change in their structure or composition.

(c) **Operating Conditions.**—The general behavior of these solutions is determined principally by the content of copper and of cyanide. It will be recalled (page 97) that the reason that complex cyanide solutions produce fine-grained deposits, and that metal is not readily deposited from them by immersion, is that in them the metal ion concentration is very low. If we assume that the copper is present as $Na_2Cu(CN)_3$, the primary dissociation of this compound may be represented as:

$$Na_2Cu(CN)_3 \leftrightarrows 2Na^+ + Cu(CN)_3^-$$

If this were the only dissociation, there would be no copper ions present in the solution, and it is doubtful whether any metal could be deposited from such a solution. A secondary dissociation, however, occurs to a slight extent, forming cuprous ions:

$$Cu(CN)_3^- \leftrightarrows Cu^+ + 3CN^-$$

That this latter dissociation is very slight is evident from the potential of copper in its cyanide solutions, from which it may be calculated that the "effective" concentration of copper ions is almost infinitesimal, about $10^{-30}N$. Such calculations are, however, subject to considerable uncertainty.[1]

With such very small concentrations of copper ions, it might seem that the actual concentration of dissolved copper would be immaterial. It is, however, because of the small content

[1] A discussion of the constitution of copper cyanide solutions will be found in GLASSTONE, S., *Jour. Chem. Soc.*, p. 702, 1929.

of copper ions that it is essential to have present a considerable concentration of dissolved copper in order to furnish new ions as fast as the copper is deposited. The actual metal concentration is, however, limited by the solubility and stability of the complex copper cyanide. For practical reasons, therefore, the metal concentration is usually maintained between 15 and 30 g./l. (2 to 4 oz./gal.), *i.e.*, the solutions are from about 0.25 *N* to 0.5 *N* in cuprous copper.

As in the cyanide solutions the copper is in the cuprous state, its electrochemical equivalent is twice as great as in sulphate solutions. It would therefore at first appear that the operation of such solutions would require less energy for the deposition of a given weight of copper. This is not the case, however, for the following reasons: In these solutions the current efficiency is rarely over 90 per cent, and is frequently below 50 per cent if the contents of free cyanide and carbonate are high. Moreover, the resistivity of these solutions is much higher than that of the acid sulphate baths, and the polarization at both the anode and cathode is greater. An e.m.f. of 4 volts may produce a current density of only about 0.5 amp./dm.^{2} (4.7 amp./sq. ft.) in cold copper cyanide solutions as compared with 8 to 10 amp./dm.^{2} (74 to 93 amp./sq. ft.) in the sulphate. In consequence the energy required to deposit a given weight of copper may be many times as great in a cyanide as in a sulphate solution, and the latter is used whenever possible.

It is necessary to have in the solutions sufficient sodium cyanide to combine with the copper to form $Na_2Cu(CN)_3$ and a certain excess, which latter is usually known as the *free cyanide*. Thus if a solution were made by dissolving 30 g./l. (4 oz./gal.) of copper cyanide and 45 g./l. (6 oz./gal.) of sodium cyanide, the copper and free cyanide contents of the resultant solution could be calculated as follows:

$$\begin{aligned} \mathrm{CuCN} : \mathrm{Cu} &= 30 : x \\ 90 : 64 &= 30 : x \end{aligned}$$

$$x = \frac{30 \times 64}{90} = 21.3 \text{ g./l. (2.8 oz./gal.) of copper}$$

$$\begin{aligned} \mathrm{CuCN} : 2\mathrm{NaCN} &= 30 : x \\ 90 : 98 &= 30 : x \end{aligned}$$

$$x = \frac{30 \times 98}{90} = 32.7 \text{ g./l. of sodium cyanide required to combine with the copper cyanide.}$$

As 45 g./l. of sodium cyanide were added, there is an excess of 45−32.7 = 12.3 g./l. (1.6 oz./gal.) of free cyanide.

It is necessary to have some excess of cyanide in the solution, otherwise when a small amount of the cyanide is converted to carbonate, the sodium cuprocyanide will be decomposed, and cuprous cyanide or hydroxide will be precipitated, causing loss of copper as sludge and also producing dark, spongy deposits. Another reason for having an excess of cyanide is that without it, anode corrosion is poor, the anode becomes coated with insoluble compounds, and the anode polarization is increased; hence it requires a higher voltage to secure the desired current density. If, however, too great an excess of sodium cyanide is present, the cathode efficiency decreases, and hydrogen in very large amount is deposited with the copper.

It is obvious, therefore, that the free cyanide content should be kept between proper limits. These can be determined by observation in any given solution by noting that sufficient cyanide is present to keep the anodes practically clean, but not enough to cause excessive "gassing" at the cathode. (There is always some gassing at the cathode in cyanide copper solutions.) The actual amount of free cyanide required depends not only on the copper content but also upon the amounts of carbonate and hydroxide present. (Hydroxide can be present only if basic carbonate has been recently added.) It has been found that as the carbonate increases, the free cyanide should also be increased in order to counteract the tendency of the carbonate to cause a coating of basic compounds on the anodes. It is partly for this reason that in copper and other cyanide solutions that have been used for long periods, more free cyanide is required than would be permissible in new solutions. It is probable that an increase in sodium hydroxide content reduces the amount of free cyanide needed. As, however, any hydroxide is converted to sodium carbonate during operation, there is not much possibility of free sodium hydroxide being present in used solutions unless it has been recently added. Practically, it is found desirable to have in freshly prepared baths a free cyanide content of from 7.5 to 20 g./l. (1 to 2.7 oz./gal.), and appreciably more in old solutions. Warm solutions require less free cyanide than cold solutions. It is customary to operate copper cyanide baths at somewhat elevated temperatures, but preferably not above 40°C. (104°F.). Much higher tem-

peratures should be avoided, as decomposition and oxidation of cyanide are thereby increased. This is objectionable because it results in loss of cyanide, precipitation of copper compounds, accumulation of sodium carbonate, and possibly in evolution of hydrocyanic acid. The use of a fairly high temperature is desirable because it increases the conductivity of the solution, improves anode corrosion, and (through the circulation produced by the heating) helps to maintain the copper concentration at the cathode.

If after long usage the carbonate content has become very high, *e.g.*, 60 g./l. (8 oz./gal.) or more, it may be reduced by the addition to the solution of a calculated amount of barium chloride. This produces an equivalent amount of sodium chloride, which is apparently less harmful than the carbonate. A method may also be used which depends upon cooling the solutions to a temperature of −5°C. (23°F.) or lower, when most of the sodium carbonate crystallizes out. Unless artificial cooling is available, this can be carried out only in very cold weather.

Solutions for *cleaning and plating* in the same operation have come into limited use.[1] The solutions employed are similar to the copper plating solutions except that they have a lower content of copper and a higher content of alkali and free cyanide. They may therefore also be considered as alkaline cyanide cleaning solutions, to which a small amount of copper has been added. They are used at a temperature of 80°C. (176°F.) or even higher, and with very high current densities. The anodes are usually of iron, or the tank itself is used as the anode. Copper compounds must therefore be added at intervals. This operation has been successfully applied to the cleaning and plating with a very thin copper coating of articles made of iron or steel and heavily coated with grease or oil or even with light rust. When such an object is made the cathode in a strongly alkaline copper solution, the grease is removed largely by the mechanical action of the gas (hydrogen) evolved upon it. Just as soon as a clean surface of iron is exposed, copper deposits upon it, but at a very low cathode efficiency, due to the high content of alkali and cyanide. The method has the advantage of carrying out quickly in one operation the cleaning and plating and of giving an indication (by the production of an adherent copper

[1] Watts, O. P., *Trans. Am. Electrochem. Soc.*, vol. 27, p. 141, 1915.

deposit) of whether the article is entirely clean. It has the disadvantage that the solution is rapidly decomposed and hence the consumption of cyanide is high, and very good ventilation is required. The energy consumption is high and the efficiency of deposition is low. The method is therefore chiefly useful in the large-scale production of cheap articles, or for the preliminary coating of iron and steel with copper.

(d) **Suggested Formulas.**—Owing partly to the difficulty of analyzing the cyanide solutions, and also to uncertainty as to the composition of commercial cyanide, the exact effect or desirable concentration of each constituent under commercial conditions has never been defined. A typical commercial formula for the preparation of copper baths is the following, in which the approximate normalities have been inserted:[1]

	Approx. *N*	g./l.	oz./gal.
Copper (cuprous) cyanide.....	0.25	22.5	3
Sodium cyanide.....	0.65	34.0	4.5
Sodium carbonate.....	0.30	15.0	2

Of the sodium cyanide used, 0.5 *N* (25 g./l., or 3.3 oz./gal.) is required to combine with the copper cyanide, and 0.15 *N* (7.5 g./l. or 1 oz./gal.) is "free cyanide."

If this bath is prepared from copper carbonate, it is necessary to use sufficient sodium cyanide to reduce as well as to dissolve the copper. This amount may be approximately calculated from the consideration of the normalities. If we assume that the basic cupric carbonate has the formula $Cu(OH)_2.CuCO_3$, its molecular weight is 221, and its equivalent weight is 55.2. In this compound the copper is cupric (Cu^{++}), and therefore to obtain an amount of copper which in the cuprous (Cu^{+}) state will produce a 0.25 *N* solution, 0.5 (and not 0.25) of the equivalent weight of the cupric compound must be used. Therefore it is necessary to employ $\frac{55.2}{2} = 27.6$ g./l. of the copper carbonate. To reduce it to the cuprous state will require the equivalent of 0.25 *N* NaCN; to convert it to cuprous cyanide 0.25 *N*; and to dissolve the cuprous cyanide 0.5 *N*; and finally to provide the free cyanide, 0.15 N. Therefore the total amount of sodium cyanide required is 0.25 + 0.25 + 0.5 + 0.15 = 1.15

[1] In this and most of the formulas suggested, the concentrations have been rounded off to a convenient number of oz./gal. and do not therefore correspond exactly to the suggested normalities.

N. As a normal solution contains 49 g./l., there will be needed $1.15 \times 49 = 57$ g./l. (7.8 oz./gal.) of sodium cyanide. As only one-half the basic copper carbonate is considered to be present as carbonate, the sodium carbonate produced in the solution will be only $1/2 \times 0.5\ N = 0.25\ N$, and to produce the same amount as was previously employed, it will be necessary to add $0.30 - 0.25 = 0.05\ N$, *i.e.*, 0.05×53 (equivalent weight of Na_2CO_3) = 2.6 g./l. of Na_2CO_3.

The formula will then be as follows:

	N	g./l.	oz./gal.
Basic copper carbonate (cupric)....	0.50	27.6	3.7
Sodium cyanide.....	1.15	57.0	7.8
Sodium carbonate.....	0.05	2.6	0.3

By this formula, a solution will be produced that is similar to the above in all respects except that it will contain a small amount (0.25 N, *i.e.*, 10 g./l., or 1.3 oz./gal.) of sodium hydroxide, which, however, as previously stated, will no doubt be converted to carbonate in a short time. For this reason it is customary in preparing the solutions from copper carbonate not to add any sodium carbonate. (Practically it is found that for some reason more cyanide is required to dissolve copper carbonate than corresponds to the above calculations.) If in the above case sodium sulphite were used to reduce the copper in the copper carbonate, it would require an amount equivalent to 0.25 N, *i.e.*, 15.8 g./l., of Na_2SO_3; and the amount of sodium cyanide would be correspondingly reduced, *i.e.*, from 1.15 to 0.90 N, or from 57 to 45 g./l., or from 7.8 to 6.0 oz./gal.

Sodium thiosulphate (hypo) is usually added in small amounts, *e.g.*, about 2 g./l., or 0.25 oz./gal., as frequently as it is needed to maintain a bright deposit. An excess should be avoided. As previously stated, a temperature of from 35 to 40°C. (95 to 104°F.) is desirable. The current density used is low, generally not over 0.3 amp./dm.^{2} (2.8 amp./sq. ft.) in cold solutions, or 1.5 amp./dm.^{2} (14 amp./sq. ft.) in warm solutions.

(e) **Analysis of Solutions.**—There is no difficulty in determining copper by the usual methods and the carbonate can be estimated with fair accuracy. The cyanide content is not, however, readily determined. It is possible and customary to titrate the "free cyanide" directly by silver nitrate, but the results secured are only a rough approximation, as they are affected

by dilution and by the presence of carbonates and hydroxides. More reproducible results are obtained by using potassium iodide to detect the end-point. The latter then corresponds approximately to the free cyanide, *i.e.* that above what is required to form $Na_2Cu(CN)_3$. The chief value of such determinations is therefore in the control of solutions, where comparative results are usually adequate. Before any thorough knowledge of cyanide copper (or brass) plating solutions can be secured, more reliable methods of analysis must be developed. In many respects it would be preferable to determine the total cyanide content of the solutions, as can be done with zinc cyanide solutions (page 332). Approximate results have been obtained by adding sulphuric acid, distilling out the hydrocyanic acid, and titrating it. So far as known, no method for determining sodium hydroxide in such solutions has even been suggested. Any such method would probably depend upon indirect calculations.

The following methods of analysis are commonly used. The solution should be filtered before any analyses are made.

Copper.—A 10-c.c. sample (or for very weak solutions 25 c.c.) is evaporated with a slight excess of dilute sulphuric acid until white fumes are produced. The addition of the sulphuric acid and the subsequent evaporation must be carried out in a well-ventilated hood, as hydrocyanic acid is evolved. If the solution becomes dark, a few drops of nitric acid should be added and evaporation continued. The residue is taken up in water, diluted to about 100 c.c., a few drops of nitric acid added, and the copper determined by electrolysis (page 217), or by the thiosulphate method (page 217).

"Free Cyanide."—A 10-c.c. sample is diluted with water to 50 c.c., 10 c.c. of 0.5 *N* potassium iodide (containing 83 g./l. of KI) is added, and a 0.1 *N* solution of silver nitrate (page 46) is run in gradually from a burette until a faint precipitate persists after vigorous shaking. The reaction which occurs is as follows:

$$2NaCN + AgNO_3 = NaAg(CN)_2 + NaNO_3$$

When sufficient silver nitrate has been added to form the soluble compound, $NaAg(CN)_2$, the next drop reacts with this compound to form an insoluble precipitate of AgI:

$$KI + AgNO_3 = AgI + KNO_3$$

The latter reaction therefore serves as an indicator of the end point of the titration. As one $AgNO_3$ molecule reacts with 2NaCN, 1 c.c. of 0.1 *N* $AgNO_3$ is equivalent to 2 c.c. of 0.1 *N* NaCN, *i.e.*, to 0.0098 g.NaCN.

Suppose that 10 c.c. of the copper solution required 14 c.c. of 0.1 *N* silver nitrate; then the solution contains:

$$14 \times 0.0098 \times \frac{1{,}000}{10} = 13.7 \text{ g./l. (1.8 oz./gal.) of "free cyanide."}$$

For the reason previously stated, it is necessary in carrying out this titration to preserve uniform conditions, otherwise the results will be erratic and not even of comparative value.

When much carbonate is present, a slight excess of barium nitrate should be added, and the precipitate of barium carbonate rapidly filtered out. The titration with silver nitrate is then carried out as above described.

Carbonate.—To 10 c.c. of the solution add about 1 c.c. of strong ammonium hydroxide (to prevent possible precipitation of copper compounds), dilute the solution to 50 c.c., heat nearly to boiling, and add an excess of a clear solution of barium nitrate, $Ba(NO_3)_2$, or barium chloride, $BaCl_2$. Allow the precipitate to settle and then filter and wash the barium carbonate with hot water. As the solutions usually contain some sulphate (which would precipitate barium sulphate), it is not possible to determine the carbonate by drying and weighing the precipitate. It should therefore be dissolved in standard hydrochloric acid and the excess of acid titrated with alkali, using methyl orange as indicator. The sodium carbonate content is then calculated from the barium carbonate found. The method is not very accurate unless carried out with special precautions, but the results are useful as an indication of the changes in carbonate content.

Suppose the barium carbonate precipitated from 10 c.c. of the solution was dissolved in 25 c.c. of 0.2 *N* HCl, and the excess of acid required 13 c.c. of 0.2 *N* NaOH to neutralize it. Then the barium carbonate was equivalent to $25 - 13 = 12$ c.c. of 0.2 *N* HCl. The carbonate content of the plating solution was therefore $\frac{12}{10} \times 0.2 = 0.24$ *N*, and the solution contained $0.24 \times 53 = 12.7$ g./l. (1.7 oz./gal.) of Na_2CO_3.

CHAPTER XIV

NICKEL DEPOSITION

1. FUNCTIONS OF CONSTITUENTS IN BATHS

Although a very great number of formulas have been employed or suggested for nickel plating, those now used are all of the same general type, *i.e.*, nearly neutral or slightly acid solutions in which the nickel is present principally as a simple salt, usually the sulphate. Nickel chloride baths were used in former years and nickel chloride is now frequently added to sulphate baths, and especially to warm nickel solutions. Ammoniacal or cyanide solutions have never been employed for nickel plating. The chief differences in the composition of commercial baths are in the exact nature or proportion of the constituents added to improve one or more properties of the solution.

Practically all of the many substances that have been used in nickel baths may be considered as serving one or more of the following purposes:

(*a*) To furnish the nickel content.
(*b*) To increase the conductivity.
(*c*) To increase or decrease the nickel ion concentration.
(*d*) To increase the anode corrosion.
(*e*) To regulate the acidity.
(*f*) To serve as "addition agents."

The principal substances used for these purposes will be considered under the above headings. Often the same compound has several functions.

(a) **To Furnish the Nickel Content.**—We may consider nickel sulphate as the essential ingredient, regardless of whether it is added as such in the form of crystals having the formula $NiSO_4.7H_2O$[1] and known as "single salts," or as nickel ammonium sulphate, $NiSO_4.(NH_4)_2SO_4.6H_2O$, the so-called "double salts." When the double salt is used, it serves simply as a source of

[1] Commercial nickel sulphate usually contains both $NiSO_4.7H_2O$ and $NiSO_4.6H_2O$.

nickel sulphate and of ammonium sulphate, which latter substance belongs in the next class of constituents to be considered The reason that these compounds are added as a double salt instead of in the form of two separate salts is that in former years the double nickel salt could be made (relatively) more cheaply than the separate nickel sulphate and ammonium sulphate, as its preparation was used as a means of recovering nickel sulphate from the "mother liquors" obtained in the crystallization of nickel sulphate. There is no reason to believe that a solution made by dissolving equivalent amounts of nickel sulphate and ammonium sulphate has any different properties than that made from nickel ammonium sulphate. The same is true of any other crystallized double salts, and therefore no added expense should be incurred simply to secure a crystallized "double salt" of any kind, except insofar as greater purity is secured. In the case of the nickel salts there is no special advantage in having the nickel sulphate and ammonium sulphate in molecular proportions, as almost invariably an excess of the nickel sulphate is used. Actually at the present time the relative prices of nickel sulphate, ammonium sulphate and nickel ammonium sulphate are such that the double salt costs more than equivalent amounts of the single salt and ammonium sulphate. In a few cases solutions have been used in which the nickel is present largely as chloride, but in general when nickel chloride ($NiCl_2.6H_2O$) is added to solutions it is used as a source of chlorine rather than of nickel.

The principal metallic *impurities* likely to be present in commercial nickel salts are iron, copper, and zinc.[1] The presence of fairly large amounts of *iron* (*e.g.*, up to 0.10 per cent Fe) is not harmful, since after operation for a short time the solution is certain to contain as much iron (especially if 95–97 per cent commercial anodes are used) as can remain in it. The amount of iron that will remain in solution depends (1) upon whether the iron is in the ferrous or ferric condition (2) upon the acidity, and (3) upon whether acids such as acetic, citric, or hydrofluoric are present. If, as is usually the case, the solutions are directly exposed to the air, or if oxygen is liberated at the anodes due to low anode efficiency, the iron will be largely oxidized to the ferric

[1] Thompson, M. R., and Thomas, C. T., The effect of impurities in nickel salts used for electrodeposition, *Trans. Am. Electrochem. Soc.*, vol. 42, p. 19, 1922.

condition. If, then, the acidity is low, *e.g.*, if the pH is above 5, the ferric salt is almost completely hydrolyzed and the iron is precipitated as ferric hydroxide, or basic ferric sulphate or borate. There is considerable uncertainty regarding the effect of small amounts of iron in nickel deposits. In one investigation[1] it was shown that nickel deposits containing iron are finer grained than pure nickel deposited under similar conditions. If, however, basic salts containing iron are included in the deposit, a porous structure may be caused. American experience does not yet justify efforts to exclude iron entirely from nickel salts or anodes, although the modern trend is toward the use of nickel anodes of high purity, which contain only small amounts of iron. When ductile nickel deposits are desired, *e.g.* for subsequent chromium plating, iron should be excluded as completely as possible.

Copper is, however, decidedly objectionable in nickel solutions, and it is probable that as little as 0.03 per cent of copper in the salt will cause dark deposits when the solutions are first operated. The reason for this behavior is that copper is appreciably below nickel in the electromotive series (Table 10) and is hence deposited more easily from these solutions than is nickel. Evidence of this relation is found in the fact that copper is deposited from such solutions upon nickel by immersion, especially if the nickel surface is clean and "active." It is quite common to find on nickel anodes a deposit of copper after they have stood in the solution some hours with no current flowing. As any copper in solution is readily precipitated, it comes down on the cathode with the first nickel deposited, and hence may be completely removed within the first few days. If, however, nickel salts containing copper are added at intervals, dark deposits are again produced.

Zinc in very small amounts is less objectionable than copper in nickel solutions and is also less likely to be present in good-quality nickel salts. Appreciable amounts were formerly found in by-product nickel salts, *i.e.*, those recovered in copper refining. As now purified, however, the by-product salts are equal in every respect to those made directly from nickel. The indications are that 0.05 per cent of zinc is detrimental and may cause inferior deposits. Excessive amounts of zinc cause black, streaky deposits and much gassing, while smaller amounts cause

[1] M. R., Thompson, The effect of iron on the electrodeposition of nickel, *Trans. Am. Electrochem. Soc.*, vol. 44, p. 359, 1923.

bright streaks, often associated with pitting. The effect of zinc may be persistent, as it does not deposit from these solutions as readily as does nickel or copper. Both zinc and copper may be almost completely removed from nickel solutions by neutralizing with calcium carbonate or hydroxide, or with ammonia to, for example, pH = 6.3, and filtering or decanting the clear solution, which should then be acidified to the desired pH. Although the reaction with calcium carbonate is relatively slow, this compound is preferable to other bases because it will not raise the pH sufficiently to precipitate nickel.

It has been recently claimed that lead is objectionable in nickel baths, although its use has also been suggested as a desirable addition agent. In any case it can not exist in a sulphate solution in any but low concentrations. If however much chloride is present, the lead is more soluble. Lead may enter the nickel solutions either from its presence in the anodes or in nickel chloride that may be used. Lead-lined tanks, which are extensively used in nickel electrotyping but not in nickel plating, may introduce traces of lead.

It has been reported by various authors that organic matter in nickel solutions may cause brittle and pitted deposits. Unfortunately there is no simple means of identifying or determining small amounts of organic matter in nickel salts or solutions. The extent to which permanganate is reduced (after all ferrous iron is oxidized) may serve as a semi-quantitative test, though hardly as a specification.

Most commercial nickel salts are nearly neutral. Occasionally, however, samples are secured which show a marked acid reaction, which is objectionable because it may cause excessive acidity of the solution and because it is an indication of lack of care in crystallization of the salts. When 10 g. of the salt are dissolved in 50 c.c. of water, the solution should produce a slightly alkaline (greenish-yellow) color with methyl red, *i.e.*, the pH should be 5.5 or above. (Pure nickel sulphate in normal solution gives a pH of 6.3.) If the salt gives a decided greenish-pink color with methyl red, the free acid may be titrated with standard alkali to a greenish-yellow color. As determined by this method, the free sulphuric acid should be less than 0.1 per cent. As much as 0.2 per cent has been found in impure nickel sulphate.

Insoluble matter in the salts is objectionable and usually indicates carelessness in the purification or handling of the salts.

In the following are summarized the specifications recently adopted by the U. S. Federal Specification Board.

Specifications for Nickel Salts

	Nickel sulphate	Nickel ammonium sulphate	Nickel chloride
Minimum content, per cent			
Nickel + Cobalt (Ni + Co)	21.4	14.6	24.3
Maximum content, per cent			
Insoluble	0.10	0.10	0.10
Free acid	0.10	0.10	0.10
Iron, Fe	0.08	0.08	0.08
Copper, Cu	0.02	0.02	0.02
Zinc, Zn	0.05	0.05	0.05

(b) **To Increase the Conductivity.**—The addition of practically any soluble sulphate or chloride to nickel sulphate will increase its conductivity. The effect upon conductivity will be greater with salts of sodium, potassium, and ammonium than with magnesium.[1] It is known[2] that the addition of magnesium sulphate to acidified zinc sulphate solutions decreases their conductivity. This is because in solutions containing considerable free acid, the conductivity is due largely to the hydrogen ions derived by dissociation of the acid, which dissociation is decreased by the addition of a sulphate, *i.e.*, a "common ion." As, however, nickel plating solutions are nearly neutral, the conductivity due to the hydrogen ions is negligible, and hence the conductivity is increased by the addition of any other sulphate. The primary function of chlorides is to aid anode corrosion, although they materially increase the conductivity. We may, therefore, consider sulphates as the principal "conducting salts." The sulphates which have been added commercially for this purpose are those of ammonium, sodium, potassium, and magnesium.

Ammonium sulphate, $(NH_4)_2SO_4$, has been most extensively used, being added as a rule in the form of "double nickel salts." The principal objection to the use of the "double salt" solutions is the limited solubility of this compound, which confines its concentration according to the temperature to from 60 to 75

[1] Hammond, L. D., *Trans. Am. Electrochem. Soc.*, vol. 45, p. 219, 1924.

[2] Tartar, H. V., and Keyes, H. E., *Jour. Ind. Eng. Chem.*, vol. 13, p. 1127, 1921

g./l. (8 to 10 oz./gal.). As this salt contains less than 15 per cent of nickel, this represents from 9 to 11 g./l. (1.2 to 1.5 oz./gal.) of nickel, and the solution is only about 0.3 to 0.4 *N* in metal. In consequence, it has been customary to add nickel sulphate to the double salt solution. In electrotyping, most of the nickel solutions formerly used contained variable proportions of "single" and "double" salts. In electroplating there has been a tendency in recent years to employ solutions consisting almost entirely of nickel sulphate and with much higher nickel concentrations than can be secured with the double salt. The fact that the presence of a small amount of ammonium sulphate has been and still is considered by many as desirable, indicates that it may serve some purpose other than increasing the conductivity. It seems probable that the presence of the ammonium ion (NH_4^+) may be of value in preventing the separation of basic nickel compounds at the cathode, because of the tendency to form ammonio-nickel complexes. The same effect is produced regardless of whether the ammonium ion is introduced through ammonium chloride or sulphate.

Of the other sulphates, magnesium sulphate ($MgSO_4$), usually purchased as Epsom salts ($MgSO_4.7H_2O$), has been most frequently used, but sodium sulphate (Na_2SO_4), which may be obtained as the anhydrous salt or in crystals of $Na_2SO_4.10H_2O$ has been used recently to increase the conductivity and throwing power, and to facilitate the nickel plating of zinc. Sodium sulphate is often used in barrel plating, where good conductivity and throwing power are especially desirable. Potassium sulphate (K_2SO_4) has been frequently suggested, but has not been applied commercially to any extent in this country. Its concentration, like that of ammonium sulphate, is restricted by the limited solubility of the double salt with nickel.

So far as is known, no strictly comparable tests have been made from which the relative merits of these sulphates, or the corresponding chlorides, can be determined. If conductivity were the only consideration, sodium sulphate would be the best sulphate, not only because of its good conductivity, but also because the solubility of the nickel sodium sulphate is greater than that of the other corresponding double sulphates, and hence a higher concentration and conductivity can be secured with it. It is possible that the nature of the alkali metal has some effect upon the character of the deposit, although Dorrance and

Gardiner[1] were unable to find any appreciable effect of the cation, *e.g.*, sodium, potassium, or ammonium that may be associated with the chloride, upon either the anode or cathode polarization. As above mentioned, ammonium salts are beneficial, especially in electrotyping solutions, as they decrease the tendency of the deposit to "burn" at high current densities. It has also been shown[2] that ammonium salts serve as buffers. Ammonium chloride is therefore usually the best form in which to add the chloride to cold solutions. In concentrated solutions for use at higher temperatures, nickel chloride is preferable, as a higher chloride content is needed than can be secured with ammonium chloride in the presence of much nickel sulphate.

(c) **To Decrease the Nickel Ion Concentration.**—The addition of sulphates to a nickel solution is advantageous not only in increasing the conductivity, but also in decreasing the nickel ion concentration. This latter effect is due primarily to the presence of the "common ion," in this case the sulphate ion (SO_4^{--}). If, for simplicity, we assume that the "mass law" holds in these concentrated solutions, it is possible to calculate roughly the change in nickel ion concentration produced by the addition of an alkali sulphate. On the basis of the common ion effect, it may be shown that the presence of N sodium sulphate in N nickel sulphate should reduce the nickel ion concentration from about 0.25 N to 0.1 N, which will have an appreciable effect upon the cathode polarization and hence upon the structure of the nickel deposit. It is at least probable that these sulphates may have a greater effect than that due to the common ion, as complex ions containing nickel may be formed. One cause of uncertainty as to the effects of these salts is the passivity of nickel (page 239) and the consequent difficulty in measuring accurately the potential of nickel in these solutions from which the nickel ion concentration might be calculated. M. R. Thompson[3] found that the addition of large amounts of sodium sulphate or magnesium sulphate greatly increases the cathode polarization in nickel solutions. This indicates that these substances also decrease the nickel ion concentration.

[1] *Trans. Am. Electrochem. Soc.*, vol. 54, p. 303, 1928.

[2] Thompson, M. R., *Trans. Am. Electrochem. Soc.*, vol. 47, p. 178, 1925; Macnaughton, D. W., and Hothersall, A. W., *Trans. Far. Soc.*, vol. 24, p. 387, 1928.

[3] *Trans. Am. Electrochem. Soc.*, vol. 47, p. 163, 1925.

The addition of citrates or tartrates to nickel solutions (such as are used for plating on zinc) causes the formation of complex nickel compounds and a reduction in the nickel ion concentration, and thus retards or prevents deposition of nickel by immersion.

(d) **To Increase Anode Corrosion.**—When pure nickel is made the anode in nickel sulphate solutions it becomes "passive," *i.e.*, its potential with respect to the solution is made more "noble," and hence it does not pass into solution at the true equilibrium potential. When the anode is passive, oxygen is discharged on its surface instead of the metal going into solution. With the low anode efficiency under these conditions, the metal content decreases, and the solution becomes acid. In consequence, the cathode efficiency decreases, poor deposits are secured, and ultimately no nickel may be deposited at the cathode. No entirely satisfactory explanation of the passivity of nickel has been made, but it appears to be due to the formation of a film of oxygen or oxide, in or on the anode surface, and to a consequent retardation in the reaction by which nickel is converted to nickel ions.

When single salt solutions are used, especially with anodes containing over 97 per cent of nickel, it is necessary to add some substance to aid anode corrosion. Those most commonly used are ammonium chloride (NH_4Cl, salammoniac) and sodium chloride (NaCl, common salt). Nickel chloride ($NiCl_2.6H_2O$) is generally used in warm solutions. In any of these salts the most essential constituent is the chloride ion (Cl^-). An excess of chloride may foster irregular corrosion and disintegration of the nickel anodes. The more sulphate there is present in the solution, either nickel sulphate or sodium sulphate, the more chloride must be used to secure good anode corrosion.

Hydrofluoric acid or fluorides have been occasionally used in nickel solutions.[1] Among the advantages claimed for such additions are better anode corrosion, and the possibility of using higher cathode current densities. The latter effect is probably connected with the formation (in the presence of boric acid) of somewhat indefinite compounds called "fluoboric acid" or "fluoborates," the presence of which serves to regulate the hydrogen ion concentration. Recently it has been found that the anode corrosion is usually less in solutions containing fluorides than in those with chlorides, especially when high purity anodes are

[1] Lovering, E. G., *Monthly Rev., Am. Electroplaters' Soc.*, vol. 8, No. 3, p. 3, 1921; Blum, W. *Trans. Am. Electrochem. Soc.*, vol. 39, p. 459, 1921.

used. The most striking behavior of fluoride solutions is their freedom from suspended sludge consisting of basic iron or nickel compounds such as are usually formed in the ordinary nickel baths. This condition is not, however, in itself evidence of better anode corrosion, but simply of the greater solubility of these compounds in the presence of fluorides or fluoborates. The term "anode corrosion" is used in different senses, but the most satisfactory definition is "the replenishment from the anodes of the metal content of the solution." Except in so far as this is accomplished, it is immaterial whether the anodes are attacked by the solution or not. Thus it is entirely possible for an anode to be attacked in such a way as to disintegrate it, but not to produce soluble compounds of the metal. From this standpoint the use of fluorides is advantageous, as practically all the metal that is attacked passes into solution instead of forming sludge. If, however, the presence of iron in the deposits is objectionable, the fluoride solutions are unsuitable, as in them practically all of the iron from the anodes passes into the deposit.

The addition of acid, and hence of hydrogen ions, is a great aid to anode corrosion and to the maintenance of clear solutions, but unfortunately the amount of acid that can be added is limited, as otherwise the cathode efficiency is decreased.

(e) **To Regulate the Acidity.**—The most striking difference in composition between the sulphate copper and the nickel depositing solutions is that the former may be used with high acid content, while the latter must be nearly neutral. In other words, copper may be deposited in the presence of a high concentration of hydrogen ions, and nickel only when the hydrogen ion concentration is low. This difference may be accounted for by considering the relative positions of copper, nickel, and hydrogen in the electromotive series (Table 10). It will be noted that copper is below hydrogen, *i.e.*, from solutions normal respectively in copper and hydrogen ions, it requires 0.34 volt higher potential at the cathode to deposit hydrogen than to deposit copper. Hence there is practically no tendency for hydrogen to be evolved from strongly acid copper solutions unless the supply of dissolved copper at the cathode becomes depleted. As this is most likely to occur when a high cathode current density is used, it follows that in acid solutions of copper the cathode efficiency tends to decrease as the current density increases.

Nickel is appreciably above hydrogen in the electromotive series, *i.e.*, it requires a higher potential (0.22 volt) at the cathode to deposit nickel from a solution normal in nickel ions than to deposit hydrogen from a solution normal in hydrogen ions. If, then, a nickel solution were strongly acidified, so that the hydrogen and nickel ion concentrations were equal, hydrogen only would be liberated at the cathode unless a very high potential (and cathode current density) was employed, in which latter case some nickel would be deposited, but in a poor physical state, due to the large amount of hydrogen simultaneously liberated. Within certain limits, therefore, in a slightly acid nickel solution the cathode efficiency increases as the current density is increased. This relation continues until the current density reaches a point where the nickel concentration at the cathode is greatly depleted, after which the cathode efficiency decreases with increased current density, just as with copper.

If, then, we assume that at any given current density the proportion of nickel and hydrogen discharged depends upon the relative concentrations of their ions in the solution, it is important to know and to control these concentrations. Roughly we may assume that in solutions which are from N to 2 N in nickel sulphate (*i.e.*, contain from 29 to 58 g./l., or 4 to 8 oz./gal., of metallic nickel) the nickel salt is ionized to the extent of about 25 per cent, *i.e.*, the actual nickel ion concentration is 0.25 N to 0.5 N.

On the other hand, there is a wide range over which the hydrogen ion concentration can be varied (page 100). For practical purposes we may consider[1] that the only range of acidity from which nickel can be deposited from still solutions is from pH = 4 to 6.3, the latter being the point at which nickel hydroxide is precipitated from sulphate solutions. The favorable range is, however, much narrower, and indications are that good results can be obtained in most solutions between pH = 5.0 and 5.5. In any

[1] Just as this edition went to press, a private communication was received from H. C. Mougey of Detroit, who found that in warm concentrated nickel solutions (*e.g.* at 140°F. or 60°C.) good nickel deposits can be obtained at high current densities (3 to 10 amp./dm.^{2} or 30 to 100 amp./sq. ft.), with a very low pH, *e.g.* 1.5 to 3.0, as measured with the quinhydrone electrode. The discussion in this text refers principally to nickel solutions at room temperature.

given solution the pH should for best results be kept within ±0.1 of the pH that has been found satisfactory.

For the reasons stated on p. 270, *it is now believed that the results of colorimetric measurements of pH are about* 0.5 *pH above those with the hydrogen electrode, which is the standard. Throughout this book, the suggested pH values have been obtained by subtracting* 0.5 *pH from those previously published, which were determined with brom cresol purple. As thus corrected, the value usually represents the standard pH within* 0.1.

The conclusions of an early study[1] of this subject may be summarized as follows:

(1) In general, good nickel deposits are produced when the cathode efficiency is high, *i.e.*, when there is little hydrogen evolved (so-called "gassing") at the cathode.

(2) Within the usual working range, the cathode current efficiency increases as the pH increases, up to about pH = 5.5.

(3) For a constant pH, the cathode efficiency increases as the current density is raised, within certain limits, which latter are dependent in part on the type of solution used.

(4) Better deposits may be secured in a solution of low pH (high acidity) at a relatively high than at a low current density.

(5) Where it is necessary to use a low current density, *e.g.*, on irregularly shaped articles, the pH should be comparatively high (low acidity).

(6) Deposits made in a solution of low pH (high acidity) are likely to be finer grained, brighter and harder, but more brittle than those from solutions with high pH.

(7) With any pH up to 4, the deposits are bright but very likely to show excessive cracking and pitting. A pH of 4 is, therefore, the lower limit of good deposition.

(8) With any pH above 6.0 the deposits are dark, and cracking and curling are likely to occur. In still solutions it is difficult to obtain good deposits above pH = 6.0. In agitated solutions, as in electrotyping, good deposits may be made up to nearly pH = 6.5.

The above conclusions were in general confirmed by observations made in a number of commercial plants before methods of measuring pH were in general use. It was found that practically all satisfactory nickel plating was conducted in solutions with a

[1] Thompson, M. R., The acidity of nickel depositing solutions, *Trans. Am. Electrochem. Soc.*, vol. 41, p. 333, 1922.

pH between 5.0 and 5.8. The average of the larger plants (in which the solutions were controlled by other analyses) was found to be about 5.3. This value is suggested for trial to those who desire to measure and control acidity in nickel plating. If fairly high current densities are used, a lower pH is generally employed, sometimes as low as 5.0. On the other hand if the bath temperature is high and only moderate current densities are used, a pH as high as 5.5 may be most satisfactory. In mechanical conveyors and in barrel plating the pH must be higher than in still solutions. The best pH must be determined for each type of bath and class of work, and then maintained closely. In agitated electrotyping solutions, the average is about 6.0 for wax molds and 5.6 for lead molds.

Although *pitting* is frequently associated with excessive acidity of the solutions, it is not correct to ascribe it entirely to that cause, as other factors may be involved, such as low nickel concentration, excessively high or low current density, the presence of dissolved gases or suspended particles in the solution, and the use of too low a temperature. It is possible to distinguish between pits which are simply depressions in the plated surface and those which consist of a depressed area with a slightly elevated ridge around it. Recently D. J. Macnaughton and A. W. Hothersall[1] made a very complete study of pitting in electrodeposited nickel. They showed that most pits are caused primarily by a minute bubble of gas, which is usually hydrogen evolved at the cathode. Pits may also be caused by oxygen which has been evolved at the anode, dissolved in the solution, and discharged at the cathode; or air which has been dissolved in the solution when it was cold and liberated when the solution was warmed by electrolysis. If the anodes are coated and hence passive, a higher potential will be required to secure the desired current density. Under these conditions there is more probability of oxygen being liberated at the anode and being carried over to the cathode. The above authors also found that defects in the base metal are very likely to cause pitting. In such cases the pitting can be reduced or eliminated by a preliminary coating of copper, upon which the overvoltage of hydrogen is higher than upon iron. The presence of zinc or of organic matter in the solution may also cause pitting. Another form of pit is probably due to the presence in the solution of finely

[1] *Trans. Far. Soc.*, vol. 24, p. 497, 1928.

suspended or even colloidal particles, such as of basic iron compounds which accumulate around the original bubble. In Fig. 28 is a good illustration of pits caused by the presence of suspended particles in the electrolytic cleaning solution, which have adhered to the cathodes.

If a well-conducting particle, such as a fragment of graphite or nickel, lodges upon the cathode, it is likely to produce an actual projection or tree, around which, especially at the beginning, a pit or crater may form, due to the excessive current density upon the projection and the consequent diversion of the current from the adjacent area. Recently C. Upthegrove and E. M. Baker[1]

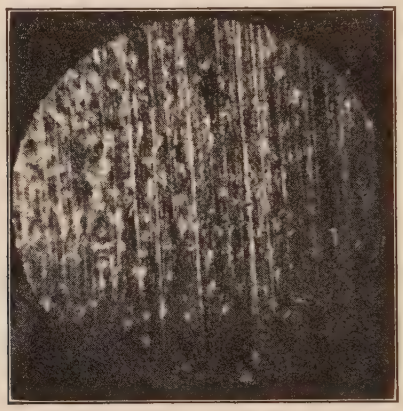


FIG. 28.—Pitted nickel deposit caused by the presence of suspended particles in the cleaning solution, and their adherence to the cathode in electrolytic cleaning.

showed that nodular nickel deposits are usually due to particles suspended in the bath, and not to imperfections in the base metal.

In view of the obvious complexity of pitting, it is certainly not safe to assume that this difficulty can be eliminated simply by controlling the hydrogen ion concentration of the solution. As, however, excessive acidity is one of the factors which may cause pitting, control of the pH will at least decrease the probability of its occurrence. It is possible by very simple tests (page 266) to measure the pH of a nickel solution, and to adjust it to any desired value (*e.g.*, 5.3) by the addition of acid if it is too high (*i.e.*, numerically above 5.3), or of ammonia if it is too low, *i.e.*,

[1] *Trans. Am. Electrochem. Soc.*, vol. 53, p. 389, 1928.

too acid (*e.g.*, below 5.3). The measurement and control of the pH of a solution should be considered as another tool, and not as a panacea for the ills of nickel plating. Even when facilities and experience are available for making chemical analyses for nickel and chlorine, frequent measurements of the acidity are desirable to supplement such analyses, and serve as a quick, convenient check upon the operations during the intervals between analyses. When no chemical analyses are available, the measurements can be readily applied as they require very little equipment or experience.

The determination of the acidity serves as an indication of any abnormal operating conditions. Under ideal conditions, with equal anode and cathode efficiencies, the pH of the solution should remain practically constant, even though the metal content has been decreased through mechanical losses. If, therefore, the solution becomes more acid, *i.e.*, the pH decreases, it is evident that the anode efficiency is lower than that at the cathode, that acid has been introduced into the bath, or that considerable iron has been oxidized, hydrolyzed, and precipitated as a basic compound. If the acidity decreases (*i.e.*, the pH increases), the efficiency at the anode is greater than at the cathode, (*i.e.*, more metal has been dissolved than deposited) or else alkali has been introduced through poor rinsing. In some cases the water used for rinsing is so alkaline that it may cause the pH to increase. Neither the pH measurement nor the nickel determination alone will show what conditions are defective, but together they give an indication of the changes required to produce uniformly satisfactory results.

The factor which determines whether the pH and the nickel concentration remain constant is not the ratio between the anode and cathode areas, but between the anode and cathode efficiencies. These efficiencies in turn are determined for any type of solution by the current densities employed. A statement of the relative anode and cathode areas has no significance unless, for example, the cathode current density is stated, in which case then the anode current density and probable efficiency can be computed. Some of the apparent anomalies and contradictions in the literature arise from failure to recognize this distinction. Thus if (*e.g.*, in a warm solution) a very high cathode current density, such as 7.5 amp./dm.^{2} (70 amp./sq. ft.), is used, and the anode area is 1.5 times as great as the cathode area, the anode current

density is very high, *i.e.*, 5 amp./dm.^{2}, (47 amp./sq. ft.), at which under only very favorable conditions can good anode efficiency be secured. If, however, as has been shown to be quite probable in rack work, the anode area is only 0.05 (1/20) that of the cathode and the average cathode current density is as low as 0.03 amp./dm.^{2} (0.28 amp./sq. ft.), the anode current density is 0.6 amp./dm.^{2} (5.6 amp./sq. ft.). At this anode current density it is not surprising that good anode corrosion is secured, even though the relative anode area is small.

If the anode efficiency is lower than the cathode efficiency, acid is set free and the pH of the solution decreases. If the initial solution contained only nickel sulphate, it will now contain nickel sulphate and sulphuric acid, and the hydrogen ion concentration will be not greatly different from that of a solution with the same content of sulphuric acid but without any nickel sulphate. In such a solution, therefore, the liberation of acid at the anode at once produces a marked effect upon the acidity or pH of the solution. If, however, a *salt* of a weak acid, such as of boric acid, is present in the solution, the liberation of a small amount of sulphuric acid simply frees a corresponding amount of the weak acid, which is so slightly dissociated that it produces very few hydrogen ions.

Solutions which contain a salt of a weak acid are said to be *buffered*, *i.e.*, they resist, so to speak, the action of acid or alkali, and maintain a relatively constant hydrogen ion concentration. The effect is much as if a reservoir of hydrogen ions were present. Other things being equal, it is obvious that a well-buffered nickel solution is desirable, as its acidity will change only slightly through appreciable changes in anode or cathode efficiency or through accidental contamination with acid or alkali.

The substance most frequently used to regulate the acidity is boric acid, which is a very weak acid. Its solubility in water at ordinary temperature is about 50 g./l. (6.7 oz./gal.). In the nickel solution it is probably somewhat less soluble. The buffer action of boric acid in a nickel solution is illustrated in Fig. 29. The curve A for nickel sulphate alone shows that the addition of only 0.5 c.c. of 0.2 *N* alkali to 50 c.c. of solution changes the pH from 4 to 6; while if 30 g./l. (4 oz./gal.) of boric acid is present (curve B) about 3.5 c.c. of alkali are required to produce the same change. (Corresponding amounts of acid would be required to produce the reverse change from pH = 6

to 4.) It is probable, therefore, that as pointed out by L. D. Hammond,[1] the chief function of the boric acid in nickel solutions is the maintenance, through its buffer action, of a constant acidity. Less than 15 g./l. (2 oz./gal.) of boric acid has very little effect on the buffer properties.

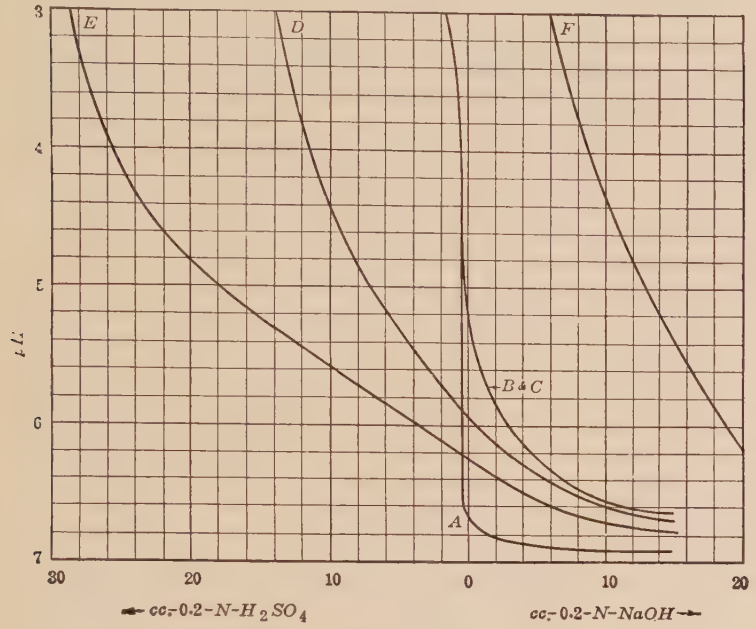


FIG. 29.—Buffer action in nickel solutions.[2]

Titration Curves for 50 c.c. of:

A—*N* $NiSO_4$
B—*N* $NiSO_4$; 0.5*M* H_3BO_3
C—*N* $NiSO_4$; 0.5*M* H_3BO_3 0.2*N* NaCl
D—*N* $NiSO_4$; 0.5*M* H_3BO_3; 0.1*N* NaF
E—*N* $NiSO_4$; 0.5*M* H_3BO_3; 0.2*N* NaF
F—*N* $NiSO_4$; 0.5*M* H_3BO_3; 0.1*N* HF

If, in addition to the boric acid, hydrofluoric acid or a fluoride is added, complex fluoboric acids are probably formed and the solution is very much better buffered than with boric acid alone. In Fig. 29, Curve *D*, it may be seen that it requires 12 c.c. of 0.2 *N* alkali to produce a change in pH from 4 to 6, *i.e.*, over three

[1] *Trans. Am. Electrochem. Soc.*, vol. 30, p. 103, 1916.

[2] The pH values on these curves are uncorrected colorimetric readings and are probably about 0.5 pH too high. As however the data on buffer action are purely relative, these figures illustrate the principles as well as do more exact data.

times as much as when only boric acid is present. This fact indicates that at least part of the beneficial action of the hydrofluoric acid in permitting higher current densities to be used is due to the buffer action of the fluoborates formed. This high buffer action of fluorides also accounts for the fact that they decrease the throwing power.

Any other weak acids will have some buffer action and thus serve to regulate the acidity. Tartaric and citric acids, used in nickel solutions for plating on zinc, and acetic acid, recently employed in solutions for producing deposits of nickel on sheet steel, all assist in the regulation of acidity. When acetic acid is used, a low pH, *e.g.*, 5.0 or less is maintained.

Weak acids such as boric acid are not suitable for making periodic adjustments of the pH. For that purpose sulphuric or hydrochloric acid should be added.

(f) **Addition Agents.**—Organic addition agents have not been extensively employed in nickel depositing solutions, not because of any lack of effect, but rather because their effects are so marked as to be difficult to control. A nickel depositing solution is very susceptible to the action of colloids. A very small amount of glue in such solutions produces cracked, curled deposits. Small amounts of dextrin, such as may be extracted by filtering a solution through cloth that has been sized, will cause very poor deposits. Gum tragacanth is used as an addition agent in nickel baths, and it is probable that other gums will have similar effects. In general, the tendency of colloids is to produce bright, brittle nickel deposits so that at most only small amounts may be present, and these must be rigidly controlled. For this reason such addition agents are not generally desirable if chromium is to be applied subsequent to the nickel.

Among other organic substances that have been proposed is glucose, which produces very bright deposits, but is difficult to control. The effect of salts of ethyl sulphuric acid (derived from ethyl alcohol and sulphuric acid), which have been used in Germany in certain solutions, probably depends upon their reducing action. None of these substances has been used to any great extent in this country.

Salts of cadmium are occasionally used as addition agents to brighten nickel deposits. They are usually introduced by suspending in the tank a small cadmium rod, which is gradually dissolved to form cadmium sulphate, though cadmium chloride

is also employed. A few observations made by H. E. Haring[1] indicate that this brightening effect of cadmium is exactly similar to that of small amounts of zinc in nickel solutions. A bright deposit can be obtained at 0.4 amp./dm.^{2} (4 amp./sq. ft.) with an addition of either 0.001 *N* Zn or Cd; *i.e.*, with 0.032 g./l. (0.004 oz./gal.) of zinc or 0.056 g./l. (0.008 oz./gal.) of cadmium. At lower current densities, or larger concentrations of these foreign metals, dark deposits form more readily with cadmium than with zinc. From these few observations it appears that zinc may be a better and safer brightening agent for nickel baths than cadmium.

Although lead is sometimes considered injurious in nickel baths, lead compounds and glycerin have been used as addition agents. The glycerin, especially in the presence of boric acid, may slightly increase the solubility of lead sulphate, in which form the lead would be otherwise almost completely precipitated from sulphate baths.

Oxidizing agents such as hydrogen peroxide, sodium peroxide, sodium perborate and potassium permanganate, are sometimes added to reduce hydrogen evolution and pitting. When present in excess they reduce the cathode efficiency and throwing power.

2. NICKEL ANODES

The operation of nickel solutions is complicated by the behavior of the anodes. As previously noted, pure nickel shows a tendency toward passivity, *i.e.*, it does not readily dissolve when made the anode. This tendency toward passivity may be reduced or overcome either by appropriate additions to the solution (p. 239). or by changing the composition or structure of the nickel anodes.

The nickel used in the preparation of cast nickel anodes is obtained usually in the form of shot or bar nickel, which contains small amounts of carbon, silicon, iron, and copper, which, however, are not present in sufficient amounts to affect the electrolytic solution pressure of the nickel. In consequence, it was formerly customary to add appreciable amounts of carbon and iron, for the combined purpose of removing passivity and of reducing the melting point. In the casting operation, silicon, manganese, and magnesium are often added as deoxidizers or degassifiers, but most of these are slagged out, and consequently the anodes contain little or no manganese or magnesium, and not much silicon.

[1] *Trans. Am. Electrochem. Soc.*, vol. 46, p. 107, 1924.

In former years nickel anodes containing only 88 to 92 per cent of nickel and from 3 to 8 per cent of iron were most frequently used. With the advent of single salt solutions containing chlorides, it was found possible to use higher purity anodes and until recently most of the anodes contained from 95 to 97 per cent of nickel. During the past few years there has been a marked increase in the use of high purity nickel anodes. These are generally specified to contain at least 99 per cent of nickel (plus cobalt) and not more than 0.35 per cent of iron, 0.10 per cent of copper, or 0.05 per cent of sulphur. As shown in the table, such anodes now contain about 99.5 per cent of nickel.

Typical Analysis of Nickel Anodes

	1	2	3	4	5	6	7	8	9
Purchased as....	90–92	95–97	95–97	95–97	95–97	99+	99+	99+	99+
Nickel and cobalt.....	91.80	97.50	97.70	97.20	97.30	99.6	99.3	99.3	99.6
Iron.....	6.41	0.60	0.90	0.55	1.18	0.25	0.38	0.36	0.30
Copper.....	0.26	0.20	0.15	0.12	0.26	0.02	0.15	0.10	
Carbon.....	1.20	1.50	0.81	1.26	0.73	0.03	0.10	.....	0.01
Silicon.....	0.22	0.05	0.24	0.18	0.38	0.02	0.01	0.13	
Manganese.....	.....	.....	.....	.....	.....	0.02	0.05		
Tin.....	.....	.....	.....	0.60					
Sulphur.....	.....	.....	.....	.....	.....	.....	0.03	0.01	
Oxygen.....	.....	.....	.....	.....	.....	.....	.....	.....	0.10
Total.....	99.89	99.85	99.70	99.91	99.85	99.94	100.02	99.90	100.01

Experience has shown that the chemical composition of a cast nickel anode, and certainly the nickel content alone, is not a criterion of its behavior upon electrolysis. One of the chief difficulties encountered is irregularity in corrosion, causing particles of uncorroded metal to detach and contaminate the solution and cause roughness of the deposits. Such difficulties are more common with pure nickel anodes than with those of lower purity. That great differences in structure may exist even in the same anode is shown by the behavior of the surface layer of rolled anodes. Sometimes this outer layer will dissolve with difficulty and may be penetrated at only a few points and subsequently drop off as a "shell." At present it is removed by the manufacturer by means of a preliminary electrolysis as anode in a 5 per cent hydro-

chloric acid solution, after which treatment the corrosion is generally uniform.

A study[1] of the behavior of anodes of different purity and source, showed that if sufficient chloride (*e.g.*, 0.25 *N*) is present, even the purest forms of nickel dissolve with high efficiencies at current densities up to 1.5 amp./dm.^{2} (14 amp./sq.ft.). Recent experience with high purity anodes, both rolled and cast, fully confirms this, in fact the pH of commercial baths with such anodes often increases and must be adjusted by additions of acid. The presence of carbon, or of nickel oxide (as in the so-called "depolarized anodes") causes the nickel to corrode more readily, *i.e.*, at a slightly lower anode potential than does pure nickel. This is probably because these insoluble substances tend to form local couples with the nickel and thus accelerate its corrosion. The presence of any insoluble material such as carbon or nickel oxide, may however cause rough deposits. The nickel oxide content should therefore be kept to the minimum that will still permit adequate anode corrosion. With sufficient chloride in the bath, perfectly pure nickel will dissolve with high efficiency.

Sulphur was found to be detrimental, as it causes disintegration of the anodes. This is because nickel sulphide separates out on the grain boundaries, and as it dissolves more easily than the nickel, particles of the latter become detached. Very small amounts of sulphur, for example 0.003 per cent, may promote uniform corrosion.

Both rolled and electrolytic anodes have been used in recent years. At present rolled anodes are more extensively used in England and America than any other kind. Rolled nickel in the usual form will corrode sufficiently to maintain the nickel content, at least in solutions containing chlorides, but there is a tendency for irregular corrosion and the detachment of particles. By suitable annealing it is possible, however, to remove strains and to alter the structure of the rolled nickel and thus to secure better and more uniform corrosion. A high chloride content also promotes uniform corrosion. Electrolytic anodes have been used successfully in solutions containing acetic acid or a large amount of chlorides. There is, however, some tendency for the detachment of flakes.

[1] Thomas, C. T., and Blum, W, *Trans. Am. Electrochem. Soc.*, vol. 45, p. 193, 1924.

3. EFFECTS OF OPERATING CONDITIONS

The reactions which occur at the anode and cathode respectively are not essentially dissimilar to those in any simple bath. We may consider that at the anode nickel is converted into nickel ions which may combine with the sulphate or chloride ion, and at the cathode the nickel ions are discharged to form metallic nickel. It appears unlikely that in mixed sulphate solutions a sufficiently large proportion of the nickel is present in the form of complex nickel anions, such as $Ni(SO_4)_2^{--}$, to alter materially the reactions in the bath. The reactions are abnormal only so far as through passivity of the anode a higher potential is required to dissolve the nickel than corresponds to its true potential, and as the cathode polarization is relatively high. the addition of various substances, such as chlorides or ammonium compounds, may reduce both the anode and cathode polarization.

It is difficult to study the exact effect of operating conditions upon the structure or properties of nickel deposits, especially those with a thickness of less than 0.001 in. (0.025 mm.), such as are commonly used in electroplating. All thin nickel deposits are so fine-grained that it is hard to detect any characteristic structure in the cross-section. The indications derived from thick deposits are, however, that the effects are similar in direction to those described in Chap. VII, *viz.*, that increasing the cathode polarization, for example by raising the current density or lowering the temperature decreases the crystal size. One reason why heated nickel solutions permit the use of a higher current density is that at the higher temperature the hydrogen which may be evolved at the cathode is less soluble in the nickel, and hence there is less tendency for the production of hard, brittle deposits.

It is difficult to state with certainty the effect of agitation in nickel solutions. Nickel electrotyping solutions, which usually have a low nickel content and a large amount of suspended basic iron sulphate, are almost universally agitated with air, and good deposits are obtained at current densities as high as 2 amp./dm.^{2} (19 amp./sq. ft.). These deposits may be somewhat rough, but this is not usually objectionable in electrotyping (p. 93). Attempts to use air agitation in nickel plating baths have not been successful, as the deposits are not only rough because of suspended matter but they also show a tendency toward cracking. The explanation of this apparent discrepancy may be

found in Bennett's theory of the "alkaline film,[1] according to which it is necessary for the liquid near the cathode to become relatively more alkaline (or, more strictly speaking, less acid) than the body of solution in order to yield a high cathode efficiency and a good deposit. He made no actual measurements of hydrogen ion concentration and hence it is difficult to define his term "alkaline." If, however, we assume that under normal conditions there is a tendency for the cathode film to become less acid than the body of the solution, it is obvious that if the solution is relatively acid, *e.g.*, pH = 5, agitation will neutralize and destroy the "alkaline film." If, however, the solution itself is nearly neutral, *e.g.*, pH = 6, agitation can have little effect upon the cathode film, as the pH of the latter can not exceed 6.0 to 6.3, in which latter range nickel hydroxide precipitates.

A study of nickel electrotyping solutions[2] showed that both the rate of covering of the nickel on the graphited wax surface and the character of the nickel deposits are influenced by the bath composition. These solutions are usually not more than 0.5 *N* in nickel, and always contain some ammonium salt. It was found that upon wax molds the best pH is from 5.8 to 6.0; while on lead molds a pH of about 5.6 is desirable.

The difficulties encountered in nickel deposition are more pronounced the thicker the deposits. In consequence, we find in descriptions of various solutions that they are or are not suitable for producing thick deposits, without, however, any clear reason for their limitations. One of the most exasperating experiences in nickel deposition is that baths prepared even on a large scale from the same or similar materials will yield different results, especially with thick deposits; or perhaps after a few weeks' operation will suddenly improve or deteriorate with no known or measurable change in their composition. It is this uncertainty which has greatly retarded the use of nickel in electroforming tubes, etc. Madsen[3] devised a method for producing thick deposits of ductile nickel, in which the cathodes are lifted from the bath at definite intervals for periods of *e.g.*, 15 seconds. Subsequently, however, he found that by the use of anodes of a different composition, developed by him, the neces-

[1] Bennett, Kenny and Dugliss, *Trans. Am. Electrochem. Soc.*, vol. 25, p. 335, 1914.

[2] Blum, W., and Winkler, J. H., *Trans. Am. Electrochem. Soc.*, vol. 53, p. 419, 1928.

[3] *Trans. Am. Electrochem. Soc.*, vol. 39, p. 269, 1921.

sity for frequent removal was decreased. In some cases at least, defective deposits are caused by the inclusion of iron or other impurities.

With many plating solutions, especially those of nickel, it is frequently found by platers that satisfactory results cannot be obtained until the solutions have been operated for one or more days. No definite explanation of this effect of "aging" has ever been established. In the case of cyanide plating solutions, the aging is undoubtedly connected with the formation of carbonates or of compounds intermediate between the cyanides and carbonates. No such explanation holds for nickel solutions as there are no marked chemical changes produced during their normal operation. It seems at least probable that the beneficial effects attributed to aging nickel solutions may be due to (*a*) an adjustment of the acidity (pH), (*b*) the formation (or precipitation) of colloids in the solution, or (*c*) a reduction in the content of dissolved air. It is at least certain that with the closer control of the purity, composition and pH of nickel solutions that has come about in recent years, the so called aging effect is less significant if not negligible.

4. DEPOSITION OF NICKEL ON ZINC, ALUMINUM, AND DIE CASTINGS

On Zinc.—When nickel is plated on such metals as zinc which is electronegative to nickel, there is a tendency for the nickel to be deposited by immersion, by such a reaction as:

$$NiSO_4 + Zn = ZnSO_4 + Ni$$

Nickel so deposited is usually black and non-adherent. In order, therefore, to produce a satisfactory deposit, it is necessary to counteract the above reaction. This is often accomplished by the use of an initially high current density. This procedure is effective provided that it produces a high cathode potential, equal to or greater than that with which the zinc tends to go into solution. The same effect may be secured by reducing the nickel ion concentration of the solution, whereby the tendency of the zinc to go into solution is decreased, and at the same time a higher potential is required for the electrodeposition of the nickel at a given current density.

In a study of the former method, *i.e.*, of increasing the initial current density, A. K. Graham[1] suggested the use of a separate "striking" bath in which a high current density is applied until the zinc is sufficiently covered with nickel that no deposition by immersion occurs when the article is transferred to the regular nickel bath. He showed that, in the striking bath used by him, it was not possible to accomplish satisfactory "striking" in any length of time at a current density of 4 amp./dm.^{2} (37 amp./sq. ft.), but that at 5 amp./dm.^{2} (47 amp./sq. ft.) 60 seconds is sufficient, and at 6 amp./dm.^{2} (56 amp./sq. ft.) 45 seconds is required to prevent any subsequent effect of the zinc when transferred to the regular bath. His striking bath consisted of:

	N	g./l.	oz./gal.
$NiSO_4.7H_2O$	0.71	108	14.5
$NiSO_4.(NH_4)_2SO_4.6H_2O$	0.25	50	6.7

M. R. Thompson[2] found that in a sulphate solution, *e.g.*, normal nickel sulphate, the single potential of zinc is about −0.8 volt. As the zinc tends to go into solution and to displace the nickel, it is necessary to apply a cathode potential of at least −0.8 volt to counteract this tendency. The essential difference between various solutions that have been used for nickel plating on zinc is in the current density at which the above potential is reached. Thus as shown in Fig. 30, in a simple nickel plating solution, a current density of at least 4 amp./dm.^{2} (37 amp./sq. ft.) must be used. If however sodium citrate is added to the solution, this decreases the nickel ion concentration and increases the cathode polarization, so that a current density of only about 1 amp./dm.^{2} (9 amp./sq. ft.) is required to reach this potential. A similar effect may be produced by adding in high concentration a salt with a common ion, such as sodium sulphate or magnesium sulphate. These have some advantages over the citrate because they are cheaper, more stable and produce a better conductivity and throwing power. One objection to them is that they increase the viscosity of the solution and hence increase the drag-out. They also decrease the anode efficiency and may cause irregular anode corrosion. No higher concentrations of sulphates should be used than are necessary to

[1] The electrodeposition of nickel on zinc, *Trans. Am. Electrochem. Soc.*, vol. 44, p. 347, 1923.

[2] *Trans. Am. Electrochem. Soc.*, vol. 47, p. 163, 1925.

prevent the appearance of black streaks in the recesses of the zinc or die-castings, at an average current density that does not produce burning on the exposed parts.

In general for nickel plating on zinc, it is desirable to use a relatively dilute nickel solution, *e.g.*, not more than about 0.5 *N*

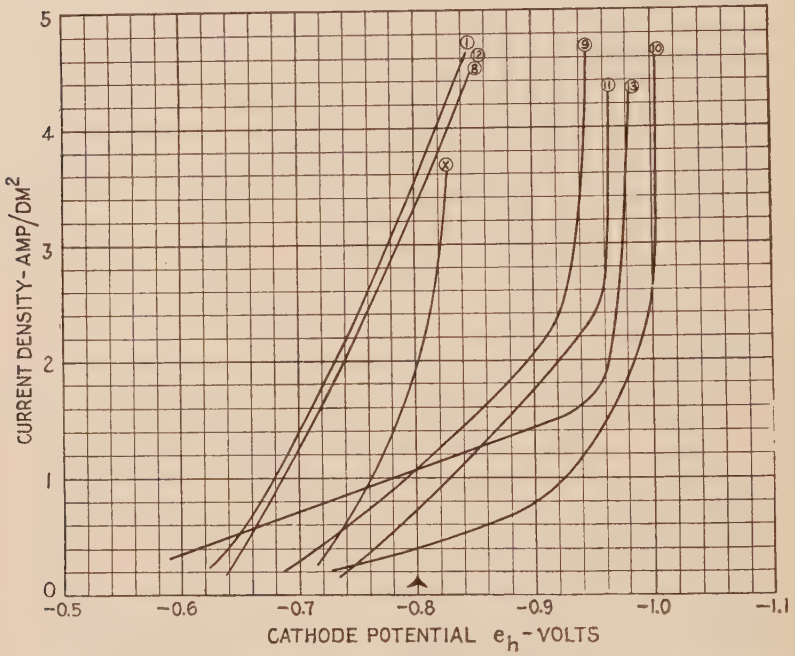


FIG. 30.—Cathode polarization curves for *normal* nickel solutions with added salts.

Curve No.	Solution
1	Standard; $NiSO_4$ — *N*; NH_4Cl — 0.25*N*, H_3BO_3 — 0.25*N*.
x	Standard at 5°C. (41°F.)
8	Standard + 0.25 *N* NaF
9	Standard + 0.50 *N* Na citrate
10	Standard + 1.0 *N* Na citrate
11	Standard + 1.0 *N* Na tartrate
12	Standard + 1.0 *N* Na acetate
13	Standard + 1.0 *N* NaH_2PO_4

(equivalent to 15 g./l. or 2 oz./gal. of metallic nickel). If this is present largely as the double salt, nickel ammonium sulphate, the ammonium sulphate thus introduced produces a beneficial common ion effect. As however the amount of double salt or of ammonium sulphate is limited by its solubility, it is usually desirable to also add a small amount of sodium citrate. In order to increase the anode corrosion and thus maintain a high pH

additional chloride may be required. No more chloride should be used than necessary, however, as this counteracts the beneficial effects of the sulphate and citrate on the cathode deposition. A bath (No. 5) which embodies these features, is included on p. 260.

Zinc Base Die Castings.—Those die castings which consist principally of zinc will behave very much like zinc but with a somewhat decreased tendency toward deposition by immersion. Their plating can therefore be accomplished with less difficulty. One of the important factors is the preliminary cleaning of the zinc or die castings, which are readily attacked by strongly alkaline solutions. For such purposes, therefore, the content of free alkali in the cleaning solutions should be kept low. Sesquicarbonate and soap are advantageous. Cleaning may be effectively done with some organic solvent such as xylene (xylol) just before introducing into a weakly alkaline electrolytic cleaner containing a soap. A dip in 10 to 20 per cent acetic acid is valuable to remove any oxides without attacking the zinc more than sufficiently to cause a slight beneficial etching action. It has also been found that a brief dip of die castings in 5 per cent sulphuric acid containing 7.5 g./l. (1 oz./gal.) of stannous chloride produces a thin film of tin, which prevents deposition of nickel by immersion.

At best the nickel plating on zinc and zinc base die castings is not entirely satisfactory, owing to the fact that if the articles are subjected to atmospheric corrosion and the base metal is exposed through porosity or abrasion, it corrodes more readily than the nickel, and therefore tends to cause blistering or peeling of the latter. If no peeling occurs, the formation of a slight white film on the nickel plated die castings, *e.g.*, automobile fittings, is usually not objectionable.

On Aluminum and Its Alloys.—At first it might appear that as aluminum is higher in the electromotive series than zinc, it should have a more marked tendency to deposit nickel by immersion. Actually, it has less tendency, probably because of the passivity of aluminum in nearly neutral solutions. The difficulties which have been experienced in securing adherent nickel plating on aluminum are apparently due to this passivity, which prevents intimate adherence of the nickel. The methods which have been successfully applied depend upon such preliminary treatment as will produce a clean but relatively rough surface upon which the adherence is therefore increased by mechanical means.

In an extensive study of nickel plating on aluminum and its alloys,[1] H. K. Work also concluded that satisfactory adherence depends upon a suitable roughening of the surface. As different alloys are attacked differently by various reagents, the most suitable etching solution must be determined for each alloy. In general the purpose should be to produce selective etching, and thus to form actual pits in the surface, which "anchor" the deposit and thus increase its adherence. It is difficult to specify the exact conditions for preparing and plating each alloy, but from the above paper the following valuable suggestions may be obtained.

Satisfactory etching of commercially pure aluminum may be accomplished with a "high nickel dip," containing 225 g./l. (30 oz./gal.) of nickel chloride, $NiCl_2.6H_2O$, (*i.e.* roughly 2 *N*) and about 10 per cent by volume of concentrated hydrochloric acid (*i.e.*, roughly *N* HCl). For the various "strong alloys" (such as duralumin), good results are usually obtained with a "manganese dip" consisting of equal parts by volume of concentrated hydrochloric acid and water, in which 4 g./l. or 0.5 oz./gal. of manganous sulphate, $MnSO_4.4H_2O$, is dissolved. For die-cast and sand-cast aluminum alloys, a strong acid dip is required, *e.g.*, one containing 3 parts by volume of concentrated nitric acid, HNO_3, and 1 part of commercial 50 per cent hydrofluoric acid, HF. In order to obtain consistent results, these dips should be maintained by regular analyses. The time required to produce satisfactory etching must be determined for each alloy and reagent, but is usually from 15 to 60 sec.

For the subsequent nickel plating, any good nickel bath is usually satisfactory, though the high sulphate or citrate baths, such as are used for plating on zinc, are preferable. A relatively high current density, at least 1 amp./dm.^{2} (10 amp./sq. ft.), should be used, as at lower current densities there is a marked tendency to produce pitted deposits on the aluminum.

Another method of preparing the surface of the aluminum involves a roughening action by the use of a sand-blast, after which the nickel plating is done in an appropriate bath. The roughening of the surface increases the adhesion, but the deposits are not so smooth as when acid dips are used.

Just as with zinc, it is difficult to produce on aluminum satisfactory deposits of nickel which will withstand atmospheric

[1] *Trans. Am. Electrochem. Soc.*, vol. 53, p. 361, 1928.

exposure. If the aluminum is exposed by abrasion, particularly in the presence of salt spray, as in a marine atmosphere, it will corrode and cause peeling of the nickel. In the research of Work it was found that the resistance to corrosion was determined by the type of alloy, the method of etching, and the adherence and porosity of the nickel.

5. SUGGESTED FORMULAS

With so many possible constituents, each of which may be used in various concentrations, it is not surprising to find a very large number of formulas in actual use, not to mention the still larger number that have been proposed in the literature. Among the many formulas which have been used successfully in commercial work are the following, which are given not as "standard" formulas, but simply as a basis for devising solutions to meet particular needs. It should be emphasized that with any nickel plating solution it is possible to greatly change the type of deposit by variations in temperature, current density and pH. The suggested conditions for each bath are simply those which most readily produce the normal deposits.

	Approx. *N*	g./l.	oz./gal.
1. *Single Salt Solution.*			
Nickel sulphate ($NiSO_4.7H_2O$)	0.75	105	14
Ammonium chloride (NH_4Cl)	0.25	15	2
Nickel chloride ($NiCl_2.6H_2O$)	0.13	15	2
Boric acid (H_3BO_3).....	0.25*M*	15	2
pH = 5.3			
Temperature, 20–30°C (68–86°F.)			
Current density, 0.5 to 2 amp./dm.^{2} (5 to 19 amp./sq. ft.)			
2. *Double Salt Solution.*			
Nickel ammonium sulphate, $NiSO_4.(NH_4)_2SO_4.6H_2O$...	0.40	75	10
Ammonium chloride (NH_4Cl)	0.25	15	2
Boric acid (H_3BO_3).....	0.25*M*	15	2
pH = 5.3			
Temperature, 20–30°C. (68–86°F.)			
Current density, 0.3 to 0.6 amp./dm.^{2} (3 to 6 amp./sq. ft.)			

3. *For Warm Solutions.*[1]

Nickel sulphate ($NiSO_4.7H_2O$)	1.40	200	27
Nickel chloride ($NiCl_2.6H_2O$)	0.40	45	6
Boric acid (H_3BO_3).....	0.5*M*	30	4

pH = 5.3
Temperature, 50–60°C. (122–140°F.)
Current Density, 1.5 to 5 amp./dm.^{2}
(14 to 47 amp./sq. ft.)

4. *For Plating on Zinc.*[2]

Nickel sulphate ($NiSO_4.7H_2O$)	0.5	70	9
Ammonium chloride (NH_4Cl)	0.25	15	2
Sodium sulphate ($Na_2SO_4.10H_2O$).....	1.0	160	22
or Sodium sulphate (Na_2SO_4)...	1.0	71	9
Boric acid (H_3BO_3).....	0.25	15	2

pH = 5.5
Temperature, 20–30°C. (68–86°F.)
Current density, 1.5 to 3 amp./dm.^{2}
(14 to 28 amp./sq. ft.)

5. *For Plating on Zinc.*[3]

Nickel ammonium sulphate ($NiSO_4.(NH_4)_2SO_4.6H_2O$)..	0.4	75	10
Sodium chloride (NaCl).....	0.7	38	5
Boric acid (H_3BO_3).....	0.25	15	2
Sodium citrate ($Na_3C_6H_5O_7.5\frac{1}{2}H_2O$).....	0.07	8	1

pH = 5.5
Temperature 20–30°C. (68–86°F.)
Current density, 1.5 to 3 amp./dm.^{2}
(14 to 28 amp./sq. ft.)

6. *For Agitated Electrotyping Solutions.* (*Wax molds*)[4]

Nickel sulphate ($NiSO_4.7H_2O$)	0.5	70.0	9.0
Ammonium chloride (NH_4Cl)	0.10	5.5	0.7

pH = 5.7
Temperature, 20–30°C., (68–86°F.)
Current density, 1 to 2 amp./dm.^{2}
(9 to 19 amp./sq. ft.)

[1] Watts, O. P., *Trans. Am. Electrochem. Soc.*, vol. 29, p. 395, 1916, recommended only 3 oz./gal. of nickel chloride. When 99+ nickel anodes are used, it is necessary to have a higher content of chloride to obtain good anode corrosion. (Hogaboom, G. B., *Met. Ind.*, vol. 27, p. 172, 1929.)

[2] Thompson, M. R., *Trans. Am. Electrochem. Soc.*, vol. 47, p. 163, 1925. A solution with twice these concentrations of nickel sulphate and sodium sulphate is useful for barrel plating.

[3] Similar to the formula of Hogaboom, G. B. quoted by Work H. in *Trans. Am. Electrochem. Soc.*, vol. 53, p. 361, 1928.

[4] For lead molds, solutions with about twice these concentrations may be used.

6. METHODS OF ANALYSIS

With the many constituents that may be present in a nickel solution, it is not feasible or necessary to make a complete chemical analysis for purposes of control. The most frequent determination made is that of nickel, while ammonia and chlorine are occasionally estimated. From these three, the ratio of single and double nickel salts and the chloride content can be calculated if the chlorine has been entirely as one of the usual chlorides, but not if chlorine has been added in two forms. The estimation of boric acid is more difficult. Magnesium can be readily determined. Fluorine can be determined with fair accuracy but the method is lengthy. Impurities in the solution, such as iron, copper, and zinc, are occasionally tested for, though usually qualitative or semi-quantitative analyses are sufficient. The acidity or pH can be quickly determined. The sodium or sulphate contents are usually not important, but if necessary, *e.g.*, for research purposes, they can be estimated.

(a) **Nickel.**—The simplest method is the electrolytic (page 39), which may be conducted either with stationary or rotating electrodes. A copper cathode may be used, but the anode must be of platinum. To 25 c.c. of the nickel solution add about 5 g. of ammonium sulphate $(NH_4)_2SO_4$, and about 25 c.c. of strong ammonium hydroxide (NH_4OH), and dilute to 200 c.c. Electrolyze with a current density of about 2 amp./dm.^{2} for about 1 hr. when the solution is agitated, *e.g.*, with a stirrer or a stream of air, or about 0.5 amp./dm.^{2} for several hours if no agitation is used. After the blue color of the solution has disappeared take out a drop of the solution and add to it a drop of a 1 per cent alcoholic solution of dimethylglyoxime, which will produce a pink color if nickel is present. Continue the electrolysis till no pink color is produced in this test; wash, dry, and weigh the cathode to determine the weight of the deposited nickel. If, *e.g.*, the increase in weight is 0.751 g., the solution contains $40 \times 0.751 = 30.0$ g./l. of nickel; or is

$$\frac{30.0}{29.3} = 1.02\ N \text{ in nickel.}$$

Nickel may also be determined by titration with a standard sodium cyanide solution. The principle of this method is that when sodium cyanide is added to an ammoniacal nickel solution, it combines with the nickel to form the double cyanide and

changes the color of the solution from a deep blue to yellow. In order to detect the end point, a precipitate of silver iodide is formed in the solution. When the cyanide is in excess, this precipitate dissolves. Sodium pyrophosphate is added to keep in solution any iron present in the sample. Citric or tartaric acid may also be used for this purpose. By having a definite small content of silver in the sodium cyanide solution, the amount of silver iodide formed and dissolved is proportional to the cyanide solution added, and no blank correction is required.

The solutions required in the method are as follows:

(1) Sodium pyrophosphate, about 0.5 *N*, containing 50 g./l. of $Na_4P_2O_7.10H_2O$.

(2) Potassium iodide, about 0.05 *N*, containing 8 g./l. of KI.

(3) Sodium cyanide solution, about 0.5 *N*, containing 25 g./l. of NaCN, to which is also added 1.7 g./l. of silver nitrate ($AgNO_3$).

To 10 c.c. of the nickel solution add 50 c.c. of the sodium pyrophosphate solution. Add ammonium hydroxide drop by drop till the solution just turns blue, and 10 c.c. of the potassium iodide solution. Titrate the solution (which should be at room temperature) with the cyanide solution until the precipitate which first forms just disappears. The cyanide solution may be standardized by means of pure electrolytic nickel, or by a nickel solution which has been analyzed electrolytically. For practical purposes a solution containing 51 g./l. of pure crystallized nickel ammonium sulphate may be assumed to contain 7.5 g./l. or 1 oz./gal. of nickel.

Example.—Suppose that a 25 c.c. portion of such a solution is titrated and requires 25.4 c.c. of the NaCN solution. Then 1 c.c. of the NaCN is equivalent to $\frac{25 \times 0.0075}{25.4} = \frac{0.188}{25.4} = 0.0074$ g. Ni. If 10 c.c. of the plating solution requires 37.5 cc. NaCN, its nickel content is $37.5 \times 0.0074 \times \frac{1000}{10} = 27.8$ g./l. (3.7 oz./gal.) and the solution is $\frac{27.8}{29.3} = 0.95$ *N* in nickel.

Nickel may also be determined colorimetrically (p. 49) by using tubes containing known concentrations of nickel sulphate. Such standards can be prepared or purchased. The use of a pink colored solution or screen to "optically neutralize" the green color is advantageous. The former is employed in Kocour's comparator, and the latter in Stirlen's nickelometer.

(b) **Ammonia.**—A 10 c.c. sample is distilled with an excess of sodium hydroxide and the liberated ammonia is passed into and absorbed by a measured volume of a solution of standard acid, *e.g.*, 25 c.c. of 0.2 *N* hydrochloric acid. The unneutralized acid is then titrated with standard alkali, using methyl orange as an indicator. From this result the volume of acid neutralized by the ammonia, and consequently the amount of ammonia present, may be calculated.

Example.—Suppose 10 c.c. of the nickel solution is distilled as above into 25 c.c. of 0.2 *N* hydrochloric acid, and the excess of the latter requires 8.4 c.c. of 0.2 *N* sodium hydroxide to neutralize it. Then the evolved ammonia must have neutralized $25 - 8.4 = 16.6$ c.c. of the hydrochloric acid. As 1 c.c. of 0.2 *N* HCl is equal to 0.0034 g. of NH_3 (*i.e.*, 0.2×0.017), the 10 c.c. of the plating solution contained $16.6 \times 0.0034 = 0.0564$ g. of NH_3, and 1 l. contains $100 \times 0.0564 = 5.64$ g. of NH_3. Or if it is desired to compute the normality directly (for subsequent calculation), this is equal to $16.6 \times 0.2 \div 10 = 0.332$ *N*.

(c) **Chloride.**—(See page 37). A 10 c.c. sample is diluted to 100 c.c., and a few drops of nitric acid are added. The solution is heated to boiling and an excess of silver nitrate is introduced. After standing, the silver chloride is filtered out on a weighed Gooch crucible, which is then dried and reweighed. From the weight of silver chloride obtained, the amount and normality of chlorine or of sodium or ammonium chloride may be computed.

Example.—Suppose that from 10 c.c. of the solution the silver chloride weighs 0.156 g.; then from 1 l. there would be produced $100 \times 0.156 = 15.6$ g. AgCl. As the equivalent weight of AgCl is 143.3, the nickel solution is $\frac{15.6}{143.3} = 0.109$ *N* in chloride, or contains $0.109 \times 35.5 = 3.87$ g./l. of chlorine.

The chloride may also be determined volumetrically by titration with silver nitrate (page 47).

In order to calculate the concentrations of the actual constituents of the solution it is necessary to know in what form the nickel, ammonia, and chlorine have been added. Let us assume in a certain case that the solution was prepared from nickel sulphate, nickel ammonium sulphate, and ammonium chloride. Then it is obvious that the content of ammonium chloride may be computed from the chlorine content. If the ammonia required to combine with this chlorine is deducted from the total ammonia, the balance of the ammonia must be present as nickel ammonium sulphate. The nickel present in the nickel ammonium sulphate

is then deducted from the total nickel present, and the balance of the nickel corresponds to the nickel sulphate present. These computations seem rather confusing, but by the consideration of the normalities, the use of cumbersome factors is avoided and the calculations are greatly simplified.

Example.—Suppose that the analysis of a solution yielded the following normalities:

$$Ni = 0.515\ N;\ NH_3 = 0.332\ N;\ Cl = 0.109\ N$$

Then the ammonium chloride must be 0.109 N, or $0.109 \times 53.5 = 5.83$ g./l. (0.78 oz./gal.).

The nickel ammonium sulphate must be $0.332 - 0.109 = 0.223\ N$, or $0.223 \times \frac{395}{2} = 44$ g./l. (5.9 oz./gal.) of $NiSO_4.(NH_4)_2SO_4.6H_2O$.

The nickel sulphate is $0.515 - 0.223 = 0.292\ N$, or $0.292 \times \frac{281}{2} = 41$ g./l. (5.5 oz./gal.) of $NiSO_4.7H_2O$.

Such calculations can be modified in accordance with the constituents used. Thus, if the chlorine has been added as sodium chloride, all the ammonia found is present as nickel ammonium sulphate. If nickel chloride has been used, an amount of nickel corresponding to the chlorine found must be deducted from the total nickel content before computing the nickel sulphate. When more than one chloride has been added, any such calculations are purely arbitrary, but may be useful for purposes of comparison.

(d) **Boric Acid.**—The following method will give approximate results for boric acid unless hydrofluoric acid or other weak acids are present. There is no simple method for determining boric acid in the presence of hydrofluoric acid.[1] The solution from which the nickel has been removed by electrolysis is filtered to remove the ferric hydroxide. It is then boiled with a slight excess of sodium hydroxide until the ammonium salts have been destroyed and ammonia is no longer evolved. A few drops of brom phenol blue or methyl orange are added and the solution is slightly acidified with sulphuric acid and is boiled until all the carbon dioxide is expelled. It is then carefully neutralized with

[1] Recently Willard H. H. and Ashworth, G. W. described to the American Electroplater's Society a method for titrating boric acid in the presence of the nickel. A red dye, fuchsin, is used to counteract the green nickel color, and the solution is saturated with mannitol and titrated with brom thymol blue as the indicator. The fluoride is removed with $CaCl_2$.

sodium hydroxide until the color of the indicator just turns. The burette reading at this point is taken as the beginning of the titration. A few drops of phenolphthalein are than added and alkali is run in until a pink color appears. About 5 g. of mannitol or 25 c.c. of glycerin are than added (which will cause the pink color to disappear) and the titration with alkali is continued until a pink color is obtained which remains after a further small addition of mannitol or glycerin. The volume of alkali added after the solution was neutralized to methyl orange is that required to titrate the boric acid, in accordance with the equation:

$$H_3BO_3 + NaOH = NaBO_2 + 2H_2O$$

(The mannitol or glycerin does not enter directly into the reaction, but serves to render the end point distinct.)

Example.—Suppose that for 25 c.c. of the solution, 14 c.c. of 0.5 *N* NaOH is required in the above titration. As 1 c.c. of 0.5 *N* NaOH is equivalent to 0.031 g. of H_3BO_3, the solution contains $40 \times 14.0 \times 0.031 = 17.4$ g./l. (2.3 oz./gal.) of boric acid.

(e) **Magnesium.**—In the solution from which nickel has been deposited electrolytically and from which the ferric hydroxide has been filtered, magnesium may be precipitated directly as $MgNH_4PO_4$ and ignited and weighed as $Mg_2P_2O_7$. To the solution add about 2 g. of ammonium chloride, and heat nearly to boiling. Add about 10 c.c. of a *N* solution of Na_2HPO_4 or $(NH_4)_2HPO_4$, then a slight excess of ammonium hydroxide, stir vigorously, and allow to stand a few hours. Filter, wash with dilute ammonium hydroxide, ignite, and weigh as $Mg_2P_2O_7$. The conversion factor from $Mg_2P_2O_7$ to $MgSO_4.7H_2O$ is 2.22.

Example.—If from 10 c.c. of the solution 0.207 g. of $Mg_2P_2O_7$ is secured, the nickel solution contains $100 \times 0.207 \times 2.22 = 46.0$ g./l. = 6.1 oz./gal. of magnesium sulphate ($MgSO_4.7H_2O$).

(f) **Fluorine.**—Fluorine can be determined in nickel solutions in the presence of boric acid by precipitation as lead chlorofluoride (PbFCl). The essential steps in the process[1] are as follows: The nickel is precipitated electrolytically in the usual way, after which the ammoniacal solution is neutralized (using brom cresol purple as the indicator) and then made 0.1 *N* in nitric acid. Lead nitrate in slight excess is added and the lead sulphate is filtered out. The solution is next neutralized with

[1] HAMMOND, L. D., *Ind. Eng. Chem.*, vol. 16, p. 938, (1924).

ammonia to about pH = 5.6, as determined with brom cresol purple, after which a saturated solution of lead chloride is added. After standing for 12 hr. the precipitate of PbFCl is filtered out on a weighed Gooch crucible (page 37) and washed with a dilute lead chloride solution and finally with water, and is dried and weighed. The factor for calculating PbFCl to NaF is 0.161.

Example.—If, from a 10 c.c. sample, 0.526 g. of PbFCl is obtained, the nickel solution contains $100 \times 0.526 \times 0.161 = 8.47$ g./l. (1.14 oz./gal.) of sodium fluoride.

(g) **Copper, Lead, Iron, and Zinc.**—Dilute 50 c.c. of the plating solution to 100 c.c. (or dissolve in 100 c.c., 10 g. of the nickel salt to be tested), and add 1 c.c. of *N* hydrochloric acid. Hydrogen sulphide is passed into the solution in a fairly rapid stream for at least 15 min. The precipitate produced will contain the copper, zinc and lead as sulphides. It is filtered out, washed with hydrogen sulphide water, dissolved in nitric acid, and the solution evaporated with sulphuric acid. The residue is treated with a little water, alcohol is added, and the precipitate of lead sulphate is weighed on a Gooch crucible. After boiling to expel the alcohol, nitric acid is added to the filtrate from the lead, and the copper is determined electrolytically. The solution from which the copper has been removed is evaporated to fumes of sulphuric acid, diluted to 50 c.c., and exactly neutralized with ammonia, for example to methyl orange. On c.c. of *N* sulphuric acid is added, the solution diluted to 100 c.c. and the zinc precipitated with hydrogen sulphide. The zinc sulphide is filtered out, ignited and weighed as zinc oxide, ZnO.

The filtrate containing the nickel and iron is boiled to expel hydrogen sulphide. A few drops of nitric acid are added and the solution is boiled to oxidize the iron, which is then precipitated with a slight excess of ammonium hydroxide, filtered, washed, ignited, and weighed as Fe_2O_3.

(h) **Acidity or Hydrogen Ion Concentration.**—pH measurements.

(1) *Hydrogen Electrode.*—As stated on p. 101, the hydrogen electrode is the primary basis of all pH measurements. Its principle is that a platinum electrode with a spongy platinum surface, when saturated with hydrogen gas and immersed in a solution, acquires a potential which is determined by the concentration (or more strictly the activity) of hydrogen ions,

i.e., the pH of the solution. This potential is measured against some standard electrode such as a "calomel electrode," by means of a potentiometer.

It is possible to make reliable pH measurements with a hydrogen electrode in many nickel plating solutions. However, the presence of small amounts of copper or lead, or of oxidizing agents in the solution leads to inaccurate values. As moreover the measurements require considerable equipment and laboratory experience, the hydrogen electrode is not well suited for measurements of commercial baths. It should be used wherever applicable for research work.

(2) *Quinhydrone Electrode.*—The principle of this method is that when a gold or platinum wire is immersed in a solution to which a small amount of quinhydrone has been added, the potential, as measured against a calomel electrode, is determined by the pH. This method is preferable to the hydrogen electrode because the measurements can be made more simply and quickly, and the results are not affected by impurities such as copper or lead that may be present in the plating baths.

It is not feasible in this brief text to describe in detail the equipment and methods used for making quinhydrone electrode measurements and computing the results. Such data will be found in "The Determination of Hydrogen Ions" (3rd ed.) by W. M. Clark, and in the catalogs of dealers in such equipment. It is now possible to obtain equipment graduated to read directly in pH. In recent years this method has been used successfully in numerous commercial nickel plating plants.[1]

(3) *Colorimetric Methods.*—The colorimetric methods are the simplest ways of measuring pH. They all involve the use of an indicator, *i.e.*, an organic dye, the color of which depends upon the pH of the solution in which it is placed. Litmus is a commonly used indicator (*e.g.*, as litmus paper), which turns blue when the pH is above 7, and pink when it is below 7. Litmus is not very sensitive to slight changes in pH, and hence other indicators are generally employed. For a given purpose an indicator should be selected that is sensitive within the range of pH to be measured. For nickel plating solutions the most suitable indicators are brom cresol purple (pH 5.2–6.8), chlor phenol red (pH 4.8–6.4) brom cresol green (pH 3.8–5.4) and

[1] PARKER, H. C., and GREER, W. N., *Trans. Am. Electrochem. Soc.*, vol. 49, p. 451, 1925.

methyl red (pH 4.2–6.3). Of these, methyl red most nearly covers the whole range of nickel plating, but its color standards are less stable than the others. Brom cresol purple has been most extensively used for nickel baths.

All of the colorimetric pH methods depend upon the addition of an indicator to the solution to be tested, and the comparison of the resultant color with that of the same indicator in a solution of known pH, or with any other standard of the same color. The four methods that have been used for such comparisons involve the following principles.[1]

(a) Buffer Indicator Tubes.—A series of standards is prepared, each consisting of a dilute buffered solution, of which the pH has been measured by the hydrogen or quinhydrone electrode. These are conveniently arranged to have intervals of 0.2 pH, for example, 5.2, 5.4, 5.6, etc. To 10 c.c. of each is added a definite volume, such as 0.5 c.c., of the appropriate indicator solution. Such color standards when hermetically sealed and protected from strong sunlight, are usually permanent for 1 year or more. These tubes are now commercially available in simple pH testing sets, such as the Lamotte set.

In using such standards, the same volume of indicator is added to 10 c.c. of the nickel bath in a tube of the same diameter. The tube is then placed in front of a tube containing water, and the transmitted color is compared with that of a color standard tube in front of a tube containing some of the *same* nickel solution. The pH of the nickel solution is then recorded as equal to that of the standard which it matches, or as the average of the two standards between which its color lies.

(b) Drop Ratio Method.—Small tubes are arranged in pairs. Into one tube are placed a number of drops of the indicator solution, for example 4, and in the other a sufficient number of drops to make the total 10; in this case 6 drops. To one tube is added a drop of dilute acid (0.05 *N* HCl), and to the other a drop of alkali (0.05 *N* NaOH). The tubes are then diluted to a definite volume, marked on each tube, for example, 5.2 c.c. When light is passed through each pair of tubes, the color corresponds to a definite pH. The pair of tubes then constitutes a color standard. The values of these are shown in the following Table. The

[1] More details will be found in Clark, W. M., "The Determination of Hydrogen Ions," 3rd ed., Williams and Wilkins Co., Baltimore, Md., 1928.

CONSTANTS FOR INDICATOR COLOR STANDARDS

Drop ratio		pH number for each pair of tubes			
Alkaline tube	Acid tube	Brom-phenol blue	Methyl red	Brom-cresol green	Brom-cresol purple
1	9	3.1	4.05	3.70	5.3
1.5(3)	8.5(17)	3.3	4.25	3.90	5.5
2	8	3.5	4.40	4.05	5.7
3	7	3.7	4.60	4.25	5.9
4	6	3.9	4.80	4.45	6.1
5	5	4.1	5.00	4.65	6.3
6	4	4.3	5.20	4.85	6.5
7	3	4.5	5.40	5.05	6.7
8	2	4.7	5.60	5.25	6.9
8.5(17)	1.5(3)	4.8	5.75	5.40	7.0
9	1	5.0	5.95	5.60	7.2

color of 5 c.c. of the nickel solution plus 10 drops of indicator is compared with these standards using some of the same nickel solution to compensate for the green color. One advantage of the drop ratio method is that the standards can be prepared without the use of any accurately standardized solutions. The colors are not very stable, and the tubes should therefore be renewed frequently. By the use of buffer solutions as recommended by Hatfield,[1] more permanent standards can be prepared.

(c) The Stirlen Wedge.—This depends upon the same principle as the drop ratio method. The acid and alkaline solutions of the indicator are in the two sides of a divided celluloid prism. Each cell is therefore in the form of a wedge, and the total thickness of the two cells at each point is the same. One portion of the nickel solution is placed in a rectangular cell back of the wedge. To another portion a definite volume of indicator is added. The prism is then moved along until a color match is obtained, when the pH is read from a scale.

(d) The Hellige Comparator.—In this instrument the color standards consists of glass discs, the color of each of which corresponds to that of the indicator at a definite pH. Nickel solution is placed in one tube, and nickel solution plus indicator in another tube. The discs are placed successively in front of the

[1] *Jour. Am. Chem. Soc.*, vol. 45, p. 940, 1923.

plain nickel solution, until as viewed with artificial light, a color match is obtained.

(4) *Relation of Colorimetric to Electrometric Readings.*—The colorimetric measurement of pH is simple and rapid, the apparatus is cheap, and the results are usually reproducible to 0.1 pH, which is adequate for the control of nickel plating baths. So long as only colorimetric measurements were employed in plating baths, no inconsistencies were observed. When however the quinhydrone electrode also came into use it was found that the colorimetric values are appreciably higher than those with the hydrogen or quinhydrone electrodes. Confusion is therefore likely to result when persons using these different methods for research or control attempt to compare or correlate their results.

Recently a cooperative study of this subject was made, the results of which were first reported to a conference held by the American Electroplaters' Society at Newark on April 6, 1929. The details of the investigation were published subsequently.[1] The principal conclusions are as follows:

(1) The results with the quinhydrone electrode are about 0.05 pH higher than the hydrogen electrode values, which latter are considered to represent the standard pH.

(2) The colorimetric readings average about 0.5 pH higher than the standard pH. The value of this deviation varies from 0.3 to 0.6 pH, according to the composition of the nickel solution, and the basis of the colorimetric method used.

(3) This "salt error" of indicators is well known. In general colorimetric standards are so prepared that they agree in value with the standard pH in dilute solutions. Most of the solutions used in other industries to which pH measurements are applied, are relatively dilute. Nickel plating solutions usually have a total salt concentration of 1 to 2 normal, and hence the discrepancy between the colorimetric and electrometric values is relatively large.

(4) The presence of iron in nickel baths causes the pH to change rapidly, and also interferes with the accurate measurement of pH by any method, electrometric or colorimetric.

(5) An increase in the temperature of the nickel baths decreases the pH however measured. This decrease in pH is more marked when ammonium salts are present. A high temperature also

[1] Blum, W., and Bekkedahl, N., *Trans. Am. Electrochem. Soc.*, vol. 56, preprint, 1929.

causes a change in the color of indicators and of the nickel solutions. *All measurements of pH should be made at normal room temperature, regardless of the temperature at which the bath is operated.*

It is difficult to devise any simple procedure for putting all pH measurements on the basis of the hydrogen electrode. *Whenever feasible the quinhydrone electrode should be used, especially for research.* For precision measurements, a deduction of 0.05 pH may be made from the quinhydrone readings.

In many commercial plants colorimetric readings will continue to prove most convenient. In such cases whenever possible, a few quinhydrone readings should also be made (*e.g.*, in some laboratory), so that the value of the correction for that type of solution may be determined. If in a given case this is 0.4 pH, this figure should be substracted from the observed colorimetric reading. Thus if the latter is 5.8, the true value is $5.8 - 0.4 = 5.4$.

When such a comparison is not feasible, or more definite data are not available, an average correction of 0.5 pH (or the specific value for a given solution as published in the above paper) may be made, in which case the revised value will probably be correct within 0.1 or possibly 0.2 pH. *In this text* (p. 242) *in order to place the previously published values (determined colorimetrically) in approximate agreement with the true pH scale,* 0.5 *pH has been deducted from each. Thus a former value of* 5.8 *is now given as* 5.3.

If the latter method is adopted, the values marked on the tubes or other color standards may be corrected by the user to read lower by 0.5 pH or whatever correction is used in that plant. If this is done, the standards should be prominently marked "for nickel plating only," so that they will not be used for dilute solutions, in which case an equal but opposite error would be made.

It should be fully realized that whether such a correction is made or not, the value of the colorimetric methods for control work in a given plant is not affected. The only justification for recommending such corrections is in order that all pH measurements in nickel plating should be on the same basis as that which is used in all branches of research and industry.

(i) **Titration of Amount of Acid (Alkali) Required.**—Measurement of the pH by means of indicators determines simply the

degree of acidity, which has a close relation to the character of the deposit produced. If, however, it is found in any case that the pH differs materially from that considered to be favorable, it is desirable to know how much acid or alkali should be added to restore the desired pH. Such information may be gained by titration of the solution with acid or alkali, using some appropriate indicator. Ordinarily, it is assumed (but not always correctly) that in such a titration the actual amount or concentration of free alkali or free acid present in the solution is determined. In the control of nickel solutions we are not usually concerned with the amount of acid or alkali present in the solution, but with the amount of alkali or acid required to "neutralize" the solution—in other words, to produce in it some desired pH. The simplest way to determine this is to titrate the solution with alkali or acid with an appropriate indicator until the desired pH is obtained. If, as has been done in some commercial plants, the solution is titrated to a sharp color change with an indicator such as sodium alizarin sulphonate or methyl red, (the neutral point of which is not the same as the pH desired), the results may be of value but not so directly as if the titration is ended at the desired pH. In the former case the solution is considered satisfactory when it has a certain definite "alkalinity;" in the latter it is satisfactory when it has the right pH, *i.e.*, does not require any acid or alkali in the titration. The degree of "alkalinity," expressed in c.c. of NH_4OH varies with the buffer properties of the solution.[1] While therefore a sharper end-point it obtained with methyl red, its relation to the desired pH is not very definite or constant, except for a given solution.

One way to titrate a nickel solution is to employ a standard nickel solution for comparison. This may be prepared by taking a few liters of a purified solution similar in composition to that in the nickel tank, and adjusting its pH by the careful addition of acid or alkali till the pH is that desired. This solution may then be filtered and preserved as a pH standard. Each time that a titration is to be made, a 50 c.c. portion of this standard is placed in a flask and 1 c.c. of the selected indicator is added. In another flask 50 c.c. of the nickel solution to be tested placed, 1 c.c. of indicator added, and the solution is

[1] Graham, A. K. A. discussion of the relation of titration and pH readings will be found in *Trans. Am. Electrochem. Soc.*, vol. 56, 1929 and *Metal Ind.* vol. 27, p. 518, 1929.

titrated with acid or alkali till the color just matches that of the standard.

Owing to the difficulty of getting a sharp end-point with brom cresol purple, it is preferable to use the quinhydrone electrode to define the correct pH for the end-point. Apparatus for this titration is now available.

Assuming that a given sample is "acid," run in 0.1 *N* sodium hydroxide from a burette, shaking the flask frequently until the color matches the standard. Each cubic centimeter of 0.1 *N* alkali used in titrating a 50 c.c. sample corresponds to 0.08 g./l. (0.011 oz./gal.) of sodium hydroxide; or to 0.12 g./l. (0.0178 fluid oz./gal.) of aqua ammonia (sp.gr. 0.9).

Example.—If, in a titration as described above, 50 c.c. of sample required 5.3 c.c. of 0.1 *N* sodium hydroxide to titrate to the desired pH, the solution will require for its neutralization:

$$5.3 \times 0.08 = 0.42 \text{ g./l. sodium hydroxide}$$

or

$$5.3 \times 0.011 = 0.058 \text{ oz./gal. sodium hydroxide}$$

For 300 gal., the total requirement would be $300 \times 0.058 = 17.4$ oz. of sodium hydroxide (stick caustic soda).

The same solution could be neutralized by adding:

$$5.3 \times 0.12 = 0.64 \text{ oz./gal. "aqua ammonia" (sp. gr. 0.9)}$$

or

$$5.3 \times 0.0178 = 0.094 \text{ fluid oz./gal. "aqua ammonia" (sp. gr 0.9)}$$

For 300 gal., the total requirement would be $300 \times 0.094 = 28.2$ fluid oz. of aqua ammonia.

Various substances may be used for neutralizing the solutions in the tanks. Nickel carbonate has the advantage that it introduces no other metals but nickel. On the other hand, its composition is somewhat indefinite and it dissolves slowly. ("Plastic" carbonate dissolves more rapidly but is still more indefinite in composition.) If slight additions are only occasionally required, caustic soda may be used in baths containing sodium chloride or sodium sulphate, or ammonia in those containing ammonium chloride. With sufficient chloride in the baths, the anode efficiency is high and the solution tends to become "alkaline," *i.e.*, to require acid to neutralize it to the desired pH. In that case sulphuric acid is usually added. It is preferable to make the additions of acid or alkali slowly, and, especially if previous experience is lacking, to add, *e.g.*, only

half the amounts calculated from the titration, and then to test the pH before adding the remainder. At best, the calculated amounts are only approximate, owing to the possible presence in the tanks of suspended impurities which may partly dissolve in and neutralize the reagent added. After each addition the solution should be well mixed and allowed to settle. Such changes are therefore best made late in the day, or at week ends.

(j) **Stripping Nickel Deposits.**—In all stripping operations it is well to move the articles or to agitate the solution in order to procure uniform action.

(1) *From Brass.*—If nickel plated brass articles are made the anode in dilute hydrochloric acid (1 part by volume of concentrated acid to 19 parts of water), a strip of lead is made the cathode, and an e.m.f. of about 6 volts is applied, the nickel will be dissolved completely in a few minutes, without any marked attack of the brass. This method is useful in determining the weight, and hence the average thickness, of the nickel. As the brass is slightly attacked, it is not possible to estimate the nickel directly from the loss in weight. The nickel must therefore be determined, *e.g.*, by the dimethylglyoxime method, in a definite portion of the solution obtained. The method is especially useful for stripping nickel from defective work prior to replating.

Another method of stripping nickel from brass is by a reverse current in 90 per cent sulphuric acid. This method has the advantage that both chromium and nickel can be stripped from brass simultaneously.

(2) *From Steel.*—The nickel plating may be dissolved from steel articles by treating them with concentrated nitric acid, which attacks the iron slightly after the nickel is dissolved. If, therefore, this method is applied for determining the weight of the nickel coating, it is necessary to determine the iron in a part of the resultant solution and to deduct the amount of iron dissolved from the total loss of weight to determine the weight of nickel. (If, as is usually the case, the nickel deposit contains not over 1 per cent of iron, this represents no appreciable error in the determination of the nickel by difference.)

Nickel may also be stripped from steel by the use of a reverse current in concentrated sulphuric acid, which should not be allowed to absorb over 5 per cent of water.

7. BLACK NICKEL PLATING

For convenience, the subject of "black nickel plating" is included in the chapter upon nickel, even though the deposits do not consist entirely of metallic nickel.

Black nickel plating may be applied directly to brass, copper, zinc, or aluminum or to steel plated with nickel, brass, copper, or zinc. Two types of black nickel baths have been used in this country, the alkaline and the acid. The former were usually prepared by adding to an ordinary nickel solution, sodium cyanide, sodium arsenite, zinc sulphate, and ammonium compounds. The formulas were often complex and frequently resulted in the formation of solutions which contained very little nickel or zinc, most of which had been precipitated as compounds present in the sludge. From such solutions it was difficult to secure a desired color and still more difficult to control the color of the deposit over considerable periods. In consequence, the use of these solutions is much less common than formerly.

A solution analogous to, but much simpler than, these alkaline black nickel solutions is the arsenic black solution. This can be prepared by dissolving arsenic trioxide in sodium cyanide. The deposits are somewhat similar to those obtained from the cyanide black nickel solutions; in fact, deposits from some of the latter may consist almost exclusively of arsenic.

The type of solution which is most extensively used for black nickel plating is the *sulphocyanate* solution, of which the following are typical formulas.

	N	g./l.	oz./gal.
(1) Nickel ammonium sulphate, $NiSO_4.(NH_4)_2SO_4.6H_2O$.....	0.30	60.0	8
Zinc sulphate ($ZnSO_4.7H_2O$)....	0.05	7.5	1
Sodium sulphocyanate (NaCNS)	0.20	15.0	2
(2) Nickel sulphate, $NiSO_4.7H_2O$...	0.5	75.0	10
Nickel ammonium sulphate, $NiSO_4.(NH_4)_2SO_4.6H_2O$.....	0.2	45.0	6
Zinc sulphate ($ZnSO_4.7H_2O$)....	0.25	37.5	5
Sodium sulphocyanate (NaCNS)	0.20	15.0	2

These solutions are operated with nickel, or nickel and carbon anodes, at a very low voltage and current density; *e.g.* from 1 to 1.5 volts between anode and cathode, producing a current density of about 0.2 amp./dm.^{2} (1.9 amp./sq. ft.). The solutions must be

kept nearly neutral, which can be done by adding ammonia if necessary. A few reported measurements of the pH of black nickel plating solutions indicate that values from 5.3 to 6.0 are satisfactory. No detailed study has been made of the effect of the pH of such solutions upon the character of the deposits.

In a brief study of the operation of a sulphocyanate solution conducted at the Bureau of Standards[1] it was found that under normal conditions the deposit contains about 50 per cent nickel, 7 per cent zinc, 15 per cent sulphur, and some unidentified organic matter. It appears probable, therefore, that it contains nickel sulphide together with some metallic nickel and zinc and an organic compound.

It is not possible to state the exact reactions that occur in the sulphocyanate bath. It seems probable that the black nickel sulphide is derived largely if not entirely from the sulphur of the sulphocyanate, which compound is decomposed upon electrolysis. The function of the zinc salt is, however, difficult to explain.

In this connection some very interesting observations were made by Joseph Haas, Jr.[2] He found it possible to produce black nickel deposits, which may have contained some nickel sulphide, by the electrolysis of solutions containing no sulphocyanate. He used a solution of the following composition; which however is not as satisfactory as the sulphocyanate solution. He found that zinc salts were essential to the produc-

	N	g./l.	oz./gal.
Nickel ammonium sulphate, $NiSO_4.(NH_4)_2SO_4.6H_2O$	0.45	90	12.0
Zinc sulphate ($ZnSO_4.7H_2O$)	0.025	4	0.5
Sodium sulphate (Na_2SO_4)	0.20	15	2.0
Sodium potassium tartrate (Rochelle salt, $NaKC_4H_4O_6$)	0.04	4	0.5

tion of the black nickel, but was unable to entirely explain the function of the zinc.

Haas also produced black deposits by electrolysis of a solution containing no sulphur, but only Rochelle salt, and the chlorides of nickel, zinc, sodium, and ammonium. It seems most probable

[1] Hogaboom, G. B., Slattery, T. F., and Ham, L. B., Black nickel plating solutions, Bureau of Standards, *Tech. Paper* 190, and *Monthly Rev., Am. Electroplaters' Soc.*, July, 1919.

[2] *Metal Ind.*, vol. 19, pp. 23, 73, 1921.

that this black deposit consisted of spongy nickel, or a mixture of nickel and zinc, possibly contaminated with basic compounds. It is not likely, however, that it could be nickelic hydroxide $Ni(OH)_3$, as suggested by Haas, as this would require an oxidizing action, such as is never observed at the cathode.

Analysis of Sulphocyanate Solutions.—The nickel and zinc may be determined after evaporating the solution with nitric acid and sulphuric acid to destroy the sulphocyanates. The residue is diluted with water, neutralized with ammonia, and then acidified with citric acid. The zinc is then precipitated with hydrogen sulphide and ignited to zinc oxide. The nickel may be determined electrolytically in the filtrate.

The sulphocyanate may be determined by adding dilute nitric acid and a measured excess of standard silver nitrate, and titrating the excess of silver with a standard solution of sodium sulphocyanate, using ferric ammonium alum as the indicator. Owing to the green color of the nickel solution it is necessary to use more ferric ammonium alum as indicator than when a colorless solution is titrated.

CHAPTER XV

COBALT AND IRON DEPOSITION

These two metals may properly be considered subsequent to nickel, as the three elements, iron, nickel, and cobalt, are not only closely related in their chemical properties but also in their electrochemical behavior. All are magnetic and show some tendency toward anode passivity and toward the absorption of hydrogen by the deposited metals. Their normal potentials in the electromotive series (Table 10, Appendix) are fairly close to each other, and all have a sufficient hydrogen overvoltage to permit them to be deposited from slightly but not excessively acid solutions. Many of the same considerations that have been discussed under nickel deposition therefore apply, at least qualitatively, to cobalt and iron. In general, baths of somewhat similar composition are used for the three metals.

1. COBALT DEPOSITION

For many years cobalt plating was regarded simply as a laboratory process, and few if any attempts were made to apply it for commercial plating, largely because of its relatively high price and the fact that all the then available supplies of the metal or its compounds could be readily utilized. A number of years ago large deposits of cobalt ores were discovered in Canada, and hence efforts were made by the government of that country to extend the applications of this metal. Among the industries considered was electroplating, and we find that the most extended researches on cobalt deposition were those conducted for the Canadian Government.[1] The discussion in this book will be confined principally to the two baths with which the best results were obtained in that work.

At the time when these results were first published, great enthusiasm was expressed over the very high current densities employed and the fine deposits secured in cobalt deposition, and

[1] Kalmus, H. T., Harper, C. H., and Savell, W. L., Electroplating with cobalt, Canada Dept. of Mines, no. 334, 1915; and *Trans. Am. Electrochem. Soc.*, vol. 27, pp. 1–43, 1915.

it was predicted by some that cobalt plating would largely supplant nickel plating. As a matter of fact, however, little if any commercial cobalt plating is now being conducted. It seems probable that the failure to employ this method is due to several causes, among which may be mentioned the following: The demand for cobalt for use in steel and other alloys has increased. In consequence, the price of cobalt has increased, while that of nickel has actually decreased. In those cases where its use was tried, it was found that cobalt oxidizes more readily than nickel, and hence it is not so suitable as nickel for plating heating appliances, such as electric irons, etc. Moreover, it does not resist the action of weak acids or other corrosive agents as well as nickel, and hence cobalt electrotypes are more readily attacked by colored inks than are nickel electrotypes. Finally, we must mention the inertia which hinders the substitution of any new process for one which depends upon long years of experience. Undoubtedly there are cases in which the commercial deposition of cobalt at very high current densities would prove advantageous, provided that enough time and energy were devoted to the adaptation of such baths to specific purposes.

The studies on cobalt deposition led to studies with similar nickel baths, and it was pointed out by O. P. Watts and others that nickel deposition can be carried out at much higher current densities than were formerly employed. In consequence, we find the use of "single salt" nickel solutions has greatly increased in recent years, with high current densities, but still no such current densities as were applied by the above authors for cobalt deposition.

Kalmus and his associates attributed the higher current densities obtainable in cobalt baths (or the lower voltage required to produce a given current density) to a better conductivity of cobalt than nickel solutions, although they made no actual conductivity measurements. Such measurements show, however, that equivalent solutions of cobalt and nickel salts, with or without corresponding additions of other salts, have almost identical conductivities. The differences in required potential must therefore be due to greater anode passivity of nickel than of cobalt, or possibly to a greater retardation of the cathode discharge in nickel than in cobalt solutions. Which of these factors is predominant could be determined only by studies of the separate anode and cathode potentials such as were not made by

these authors. That the anode polarization is greater with nickel than with cobalt is indicated by their own observations upon the more ready solubility of the cobalt anodes. It is probable that the cathode polarization is also lower in cobalt than in nickel solutions.

Many of the statements in the literature regarding the hardness of electrodeposited metals are based upon tests upon these metals in the cast or rolled condition. It is by no means certain that the hardness of electrodeposited metals is parallel to their hardness in other forms. Moreover, the hardness of any given electrolytically deposited metal is determined largely by the conditions of its deposition, such as current density, temperature, and composition of the solutions. If, therefore, the cobalt deposits secured by Kalmus were harder than nickel, it may have been due principally to the fact that higher current densities were used than with nickel.

1. Suggested Formulas

The two baths which they recommended most highly, designated by them respectively as "I B" and "XIII B," had the following compositions. (The above authors expressed their results in terms of the weight of salts dissolved in a liter of *water*. For convenience, these results have been recalculated in terms of the weight per liter of *solution*, using the specific gravities given by the authors.)

Solution I B

	N	g./l.	oz./gal.
Cobalt ammonium sulphate $CoSO_4.(NH_4)_2SO_4.6H_2O$	0.96	175	24.0
Sp. gr. = 1.053			

Solution XIII B

Cobalt sulphate ($CoSO_4$)	3.60	278	37.0
or Cobalt sulphate ($CoSO_4.7H_2O$)	3.60	504	68.0
Sodium chloride	0.30	17	2.3
Boric acid, nearly to saturation ∴ probably about	0.75*M*	45	6.0
Sp. gr. = 1.24			

Consideration of bath I B, which is a nearly saturated solution of the double salt, cobalt ammonium sulphate, indicates that it owes at least part of its advantages to the greater solubility of this salt than of the corresponding nickel salt. With this bath the above authors obtained satisfactory deposits with cur-

rent densities as high as 4 amp./dm.^{2} (37 amp./sq. ft.), which is considerably higher than has been found practicable with double nickel salt solutions. The function of the ammonium sulphate may be assumed to be the same as in nickel baths, *i.e.*, to increase the conductivity, decrease metal ion concentration, and possibly to aid anode corrosion.

In the bath XIII B, we have (*a*) a high concentration of cobalt (but no higher than can be obtained with nickel sulphate); (*b*) a small amount of a chloride to improve anode corrosion; and (*c*) a considerable amount of boric acid to regulate the acidity through its buffer action. In Kalmus' experiments frequent reference is made to the reaction of the solutions, but not in quantitative terms. Thus his solution I B is reported even after long operation to be "neutral to litmus paper but very slightly alkaline as shown by titration with $\frac{N}{10}$ HCl and litmus indicator." His solution XIII B is reported as "strongly acid to litmus," which indicates that the pH of the solution was less than 6 and possibly less than 5. In a study[1] of the pH of cobalt solutions it was found that the favorable range is similar to that in nickel baths. With bath XIII B very high current densities were successfully applied, and good deposits were obtained at current densities ranging from 3.5 to 17.5 amp./dm.^{2} (33 to 163 amp./sq. ft.), which latter value is much in excess of what has ever been applied in nickel solutions under similar conditions, *i.e.*, at ordinary temperature and without agitation.

The above authors used successfully both cast and rolled cobalt anodes, containing from 96 to 98 per cent of cobalt, and small amounts of nickel, iron, carbon, silicon, and other usual impurities. Because of the more ready solubility of cobalt, the rolled anodes corrode even more easily than do rolled nickel anodes.

2. Analysis of Solutions

The methods of analysis of cobalt solutions are essentially similar to those for nickel; in fact, in the usual electrolytic method for determining nickel, any cobalt present is weighed with the nickel. Unless otherwise stated, therefore, the results of an electroanalysis of a nickel or a cobalt solution include both

[1] Montillon, G. H., and Cassel, N. S., *Trans. Amer. Electrochem. Soc.*, vol. 45, p. 259, 1924.

metals. Methods for the separation of cobalt and nickel are rather complicated and will not be described here.

2. IRON DEPOSITION

Although it has been known since 1860 that iron can be deposited from its solutions, the process has found very little commercial application except in the refining of iron, *i.e.*, the preparation of pure iron for special purposes. It was used for some time in Russia for making or coating printing plates, for which it seems to have had a suitable hardness. In recent years, interest in iron deposition has been renewed because of its successful application during the war for building up worn or undersized parts of military equipment. An excellent summary of the "Researches upon the Electrodeposition of Iron" from 1860 to the present was published[1] by W. E. Hughes, who has himself made notable contributions to the subject.

In view of the cheapness and availability of iron, some surprise has been expressed that its deposition has not been more extensively applied for purposes other than refining. The reasons for this apparent neglect of iron deposition are not, however, difficult to find. Iron plating is not deserving of consideration for either protection or appearance, because of the ready corrodibility of iron, especially the electrolytic iron. Since a large part of the plating industry involves the coating of iron or steel with other metals for decoration or protection, there is little field for iron plating for such purposes. In the manufacture of printing plates there has been a demand in recent years for a surface more durable than copper. This demand has been met so successfully by the use of nickel that it is now not unusual to secure as many as 2,000,000 impressions from a nickel electrotype, a number which is greater than is usually desired except in unusual cases, such as the printing of government securities, cartons, bread wrappers, etc. For such demands or for printing on leather or rough cardboard, etc., it is admittedly desirable to secure harder surfaces, which is now being successfully accomplished by means of chromium. Iron deposition, possibly followed by case-hardening, may be advantageous for specific purposes. Any such development will usually depend upon a definitely superior service of the iron,

[1] *Trans. Am. Electrochem. Soc.*, vol. 40, pp 15–53, 1921.

and not upon its cheapness. On an ordinary nickel electrotype the actual cost of the nickel surface (which is usually less than 0.025 mm., or 0.001 in. thick) is much less than 1 per cent of the cost of the finished plate, so there would be relatively little economy in the substitution of iron for nickel. For very thick plates however the smaller cost of the iron may represent a real economy.

Even in that field in which the process was recently used successfully, *i.e.*, the building up of parts, there is no evidence that the deposited iron is necessarily harder than nickel, and it is probable that nickel might have been used for this purpose if adequate supplies of it had been available in England and France. In America, nickel was not infrequently deposited upon undersized shells or other equipment. The greater experience of practical platers with nickel deposition made its application immediately possible without the necessity of extended research. Now, however, as the result of extensive studies, a large fund of information has been secured, and after greater practical experience it appears probable that iron deposition will be extensively used. Whenever large-scale operation is involved, the lower cost of the iron and iron compounds and the use of high current densities favor the use of iron.[1] In those applications in which case-hardening is practicable, iron deposits have a unique value. Electrolytic iron tubes have been successfully produced abroad, and in recent years electroforming with iron has also been investigated in this country[2] and in Canada.[3] Thus far however it has not proven practicable in America to produce electrolytic iron tubes at a price to compete with drawn tubes. Further research and development will be required to yield success in this field.

Iron depositing baths possess most of the characteristics and show many of the same defects as nickel baths, and in addition have the disadvantage that there is tendency for ferrous (Fe^{+II}) salts to oxidize to ferric (Fe^{+III}), especially when the solutions are nearly neutral. In consequence, the solutions tend to change in composition, and especially in acidity, and require rather fre-

[1] Hughes, W. E., *Chem. Met. Eng.*, vol. 26, p. 267, 1922.

[2] Stoughton, Bradley, *Chem. Met. Eng.*, vol. 26, p. 128, 1922; and Belcher, D., *Trans. Am. Electrochem. Soc.*, vol. 45, p. 455, 1924.

[3] Trail, K. J. and McClelland, W. R., *Can. Dept. Mines, Pub.* 670, p. 72, 1926.

quent regulation. The work of Hughes,[1] McFadyen,[2] Alley,[3] and others in recent years has shown that it is possible under properly controlled conditions to produce dense, fine-grained iron deposits; but they have also shown the marked tendency of iron to form cracked, pitted, or spongy deposits, or those containing oxide inclusions. Careful control of the solutions is therefore essential.

1. Suggested Formulas

Practically all of the numerous iron baths contain ferrous sulphate or chloride or both. As summarized by Hughes, the chloride baths have the advantage of greater solubility, better conductivity, and higher permissible current densities. The sulphate baths, however, can be operated at ordinary temperature, while the chloride require elevated temperatures. The sulphate baths and the iron deposited from them oxidize less readily than do the chloride baths or deposits.

The "Fischer-Langbein" solution is probably the most satisfactory chloride bath. The original formula is

Ferrous chloride ($FeCl_2.4H_2O$)	450 g.
Calcium chloride ($CaCl_2$)	500 g.
Water	750 c.c.

If, as stated by Hughes[4] the volume of the solution is about twice that of the water, these amounts will produce about 1.5 l. of solution. The formula may therefore be expressed as follows:

	N	g./l.	oz./gal.
Ferrous chloride, $FeCl_2.4H_2O$	3	300	40
Calcium chloride, $CaCl_2$	6	335	45

The bath is operated at 90°C. (194°F.) to 110°C. (230°F.) at current densities up to 20 amp./dm.^{2} (186 amp./sq. ft.). In this

[1] Electrodeposition of iron, Dept. Sci. & Ind. Res., London, *Bull. 6*, 1922.

[2] *Trans. Far. Soc.*, vol. 15, p. 98, 1920.

[3] *Machinery*, vol. 30, p. 202, 1923; and *Brass World*, vol. 19, p. 373, 1923.

[4] *Brass World*, vol. 18, p. 261, 1922. A recalculation of Hughes' data, including the specific gravity of the solution, shows that the volume of the bath was not more than about 1.6 times that of the water. The solution formula given here is therefore somewhat less concentrated than that employed by Hughes. As the latter bath was supersaturated at ordinary temperature, it is more convenient to employ the somewhat lower concentration, as has been done in experiments of C. T. Thomas which will be referred to.

bath the stated function of the calcium chloride (or sodium chloride, which has also been employed) is to decrease the evaporation and oxidation of the solution. In addition it also increases the conductivity and decreases the metal ion concentration.

Recent experiments of C. T. Thomas and W. Blum at the Bureau of Engraving and Printing show that a bath such as the above is very satisfactory for making thick deposits of iron, *e.g.* for printing plates. The bath contains in addition to the ferrous chloride and calcium chloride, about 0.01 to 0.02 *N* free hydrochloric acid. The pH as measured with a quinhydrone electrode is about 1.8. The solution is kept in a rubber lined iron tank or a tank lined with acid proof brick. The anodes, consisting of rolled "armco" iron, are contained in porous alundum pots, which prevent any anode sludge from reaching the cathodes. A temperature of about 90°C. (194°F.) and a current density of about 6.5 amp./dm.^{2} (60 amp./sq. ft.) are used. Deposits over 5 mm. (0.20 in.) thick are relatively smooth, and fairly ductile. The tensile strength of the iron is about 4,000 kg./cm.^{2} (56,000 lb./sq. in.) and the elongation about 20 per cent. The cathodes are moved mechanically during the deposition.

A sulphate bath recommended by McFadyen was extensively used during the war. Its composition is very simple, *viz.*, a 1.8 *N* solution, *i.e.*, 350 g./l. (47 oz./gal.) of ferrous ammonium sulphate, $FeSO_4.(NH_4)_2SO_4.6H_2O$, analogous to the double nickel salt. It is slightly acidified with sulphuric acid, *i.e.*, about 0.005 *N*, or 0.25 g./l. (0.03 oz./gal.) of sulphuric acid. It is used at ordinary temperature with a current density of about 2 amp./dm.^{2} (19 amp./sq. ft.).

Probably the acidity or hydrogen ion concentration is more important than any other single factor in iron deposition, not only because of its direct effect upon the cathode efficiency and character of the deposit, but also because of its relation to the rate of oxidation of the ferrous salt and the precipitation of basic ferric salts. Almost all authors have recommended a "slightly acid" solution, but a few have specified that it should be "neutral." But these terms are only relative, depending upon the method of measurement or observation. Recently the process of depositing iron on undersized parts was described by D. R. Kellogg,[1] who made observations upon the pH of sulphate solutions and obtained good deposits at about pH = 6. This was

[1] *The Electric Jour.*, vol. 19, p. 249, 1922.

maintained by keeping ferrous carbonate in suspension in the baths. In the chloride bath however a greater acidity, corresponding to about 0.01 to 0.02 N HCl, or a pH from 1.5 to 2.0, is desirable.

2. Analysis of Solutions

The determination of the ferrous iron in such solutions can be readily accomplished by a direct titration with potassium permanganate, after the addition of sulphuric acid to the sulphate solutions, or of the manganous sulphate titrating mixture to chloride solutions. The permanganate solution should be standardized with sodium oxalate for accurate work, but for testing the iron plating solutions standardization against pure ferrous ammonium sulphate is sufficiently accurate.

For a sulphate solution, a 5-c.c. sample is diluted to 50 c.c., 10 c.c. of concentrated sulphuric acid added, and the solution is titrated with $\frac{N}{2}$ $KMnO_4$ to the appearance of a permanent pink color. For a chloride solution the same method is used except that instead of sulphuric acid, 25 c.c. of a titrating mixture is introduced. Each liter of this contains 100 g. of crystallized manganous sulphate, 300 c.c. of 85 per cent phosphoric acid and 150 c.c. of concentrated sulphuric acid. The solution is then titrated to a pink color.

Example.—Suppose 2.10 g. of pure ferrous ammonium sulphate, when dissolved and titrated, requires 22.0 c.c. of $KMnO_4$ solution (containing 16 g./l. $KMnO_4$). Ferrous ammonium sulphate contains just 1/7 of iron. Therefore

$$2.10 \text{ g.} = 2.10/7 = 0.30 \text{ g. Fe; and 1 c.c. of } KMnO_4 = \frac{0.30}{22.0} = 0.0136 \text{ g. Fe}$$

If 5 c.c. of the plating solution requires 30.4 c.c. of $KMnO_4$, the bath contains

$$30.4 \times 0.0136 \times 1{,}000/5 = 82.6 \text{ g./l. Fe.}$$

A normal solution of a ferrous salt contains $56/2 = 28$ g./l. Fe. Therefore the solution is $82.6/28 = 2.9$ N in ferrous salt.

In chloride solutions the *ferrous iron* may also be determined by titration with a standard dichromate solution, using diphenylamine as an inside indicator.

The *free acid* may be titrated with 0.1 N sodium hydroxide. To 25 c.c. of the solution, without dilution, several drops of

brom phenol blue are added, and then the sodium hydroxide is run in till a bluish color is produced. Small amounts of ferric iron that may be present tend to obscure the end point, which can be detected with practice. If, as is the case in most solutions during satisfactory operation, the content of ferric iron is very low, no appreciable effect is produced on the acidity titration. If much ferric iron is present it must be determined, and its equivalent of alkali deducted from that used in the titration.

The *chloride* may be determined by the silver nitrate titration (p. 47), after the iron has been oxidized and precipitated as ferric hydroxide by sodium hydroxide.

The *calcium* can be most readily computed from the specific gravity and the content of ferrous chloride. The necessary data are shown in Table 15 in the Appendix.

Example.—Suppose that the solution titrated above contains 2.9 *N* ferrous chloride and has a specific gravity of 1.35. From Table 15 (appendix) it may be seen that a 3 *N* ferrous chloride solution containing 5 *N* calcium chloride, has a specific gravity of 1.35. Hence the bath is approximately 5 *N* in $CaCl_2$ or contains 278 g./l. or 37 oz./gal. of $CaCl_2$.

CHAPTER XVI

CHROMIUM DEPOSITION

1. COMPOSITION OF THE SOLUTIONS

To a chemist, the most striking characteristic of the chromic acid solutions that are almost universally employed for chromium plating, is that in chromic acid, CrO_3, (or more strictly speaking "chromic anhydride") the valence of the chromium is six. In consequence it would require at 100 per cent cathode efficiency about three times as many ampere hours to deposit a given weight of chromium as it does for copper from a sulphate solution, in which the valence of copper is two; and about six times as much as it does for copper from a cyanide solution in which the valence of copper is one. As however, the cathode efficiency of chromium deposition from chromic acid is almost always less than 20 per cent, it is evident that chromium requires about 15 times as many ampere hours as does the same weight or thickness of copper or of nickel from sulphate solutions. The question may be asked therefore why chromic acid baths are used instead of those containing a simple salt of chromium, such as chromium chloride or sulphate, in which the valence of chromium is three.

It has long been known that chromium can be deposited from its simple salt solutions such as the chloride or sulphate, but in spite of numerous researches on this subject, such solutions have never come into extensive commercial use. The two principal difficulties encountered are (1) the maintenance of a high anode efficiency with chromium anodes and (2) the control of the pH so as to prevent hydrolysis and precipitation of chromium hydroxide or basic salts, and still permit a high cathode efficiency. Pure chromium anodes tend to become passive at high current densities, even in chloride solutions; under which conditions chromic acid may be formed. Unless the anode efficiency is high, some of the trivalent chromium present, *e.g.*, as chromium chloride ($CrCl_3$) may be oxidized to chromic acid, producing a bath that is less stable and may have a lower cathode efficiency than the regular chromic acid bath. It is also known that

chromium salts such as chromic chloride and sulphate may exist in two forms, *i.e.*, the violet and the green modifications. Of these, the green salts hydrolyze more readily, *i.e.*, at a lower pH, and are consequently less stable than the violet. The successful operation of chromium chloride baths will therefore depend upon overcoming the passivity of chromium anodes, and of maintaining permanently a violet solution, at such a pH as will permit a high cathode efficiency at a reasonable current density. While some promising results with such baths have been reported recently, no details have been published from which the operating conditions might be defined.

For the present therefore discussion must be confined to the chromic acid bath that is now in extensive use. The use of this bath dates back to 1857, when chromium was deposited from chromic acid by Geuther in Germany. Since that time there have been many investigations of chromium plating, but in spite of the very good deposits obtained by many early workers, it has only been within the past 10 years that these baths have been successfully operated upon a commercial scale. Without attempting to discuss the merits of the numerous papers and patents upon this subject,[1] it appears probable that the recent advances have been largely due to (1) a greatly increased demand for an attractive metallic finish on automobiles that will have a more permanent luster than nickel surfaces; and (2) the increased knowledge and experience with the scientific operation of all plating processes, which have facilitated that closer control of plating conditions which is essential for success in chromium plating. Almost all the baths now used have chromic acid as their principal constituent, with a small amount of some other compound such as a sulphate. In various published formulas, the sulphate ion has been introduced by the addition of sulphuric acid or of sulphates such as those of chromium, sodium, potassium, ammonium, magnesium, and nickel. In addition

[1] A comprehensive study of the patents on chromium plating was published by R. Schneidewind, in University of Michigan *Engineering Research Bulletin*, No. 8, 1927. A summary of the literature on chromium plating, including some previously unpublished researches of the above author, was also published by Schneidewind in University of Michigan *Engineering Research Bulletin*, No. 10, 1928. As these are both readily available, no attempt will be made in this text to discuss the history of chromium plating or the details of researches. Instead, an effort will be made to summarize the important conclusions of the researches and the present status of the process.

basic substances such as chromic hydroxide or carbonate have been recommended, as well as iron, which is introduced in the form of ferrous sulphate or of ferric chromate. In consequence a large number of formulas have been proposed, and it is impossible to discuss all of them critically, owing to the lack of quantitative information on many points.

In an extensive study of this subject, H. E. Haring and W. P. Barrows[1] compared the behavior of baths containing in addition to chromic acid, equivalent amounts of (*a*) free sulphuric acid, (*b*) chromium sulphate, and (*c*) chromium sulphate plus a small amount of basic material present as "chromium chromate" (produced by the addition of chromium carbonate to the solution). They came to the conclusion that, for the same content of sulphate (SO_4) these three types of bath are identical in cathode polarization and cathode efficiency, and that the principal effect of the chromium chromate is that it reduces the conductivity of the solution. The range of current density and temperature within which bright deposits are obtained was found to be the same for all three solutions.

It is apparent that the only essential constituents are chromic acid and a sulphate. Identical results are obtained regardless of the form in which the sulphate is introduced. The simplest and most definite form in which to add the sulphate is as sulphuric acid. The above authors found that the highest cathode efficiency is obtained when the ratio by weight of chromic acid (CrO_3) to sulphate (SO_4) is about 100:1. As shown on p. 299, however, a slightly better throwing power is obtained with a ratio of about 200:1. Too low a sulphate content causes brown streaks on the deposit. The concentration of chromic acid in commercial baths varies from about 180 g./l. (24 oz./gal.) to 480 g./l. (64 oz./gal.). A higher cathode efficiency is obtained with the more dilute solutions, of which however the resistivity is greater than that of concentrated solutions. For most purposes therefore an intermediate concentration, *e.g.*, 250 to 300 g./l. (33 to 40 oz./gal.) of chromic acid is satisfactory, if an adequate voltage is available. For such baths the corresponding concentrations of sulphuric acid (or of sulphate ion, SO_4) for a 100:1 ratio would be 2.5 to 3 g./l. (0.33 to 0.4 oz./gal.).

The calculation of the equivalent concentrations of other sulphates to replace the sulphuric acid can be done most conven-

[1] Bureau of Standards, *Technologic Paper*, 346, 1927.

iently by considering the normalities of the solutions. The equivalent weight of sulphuric acid is 49, *i.e.*, 98/2. Hence a solution containing 2.5 g./l. is equal to 2.5/49 = approximately 0.05 *N*. The molecular weight of chromium sulphate, $Cr_2(SO_4)_3$ is 392. As each atom of chromium has a valence of three, the equivalent weight is equal to $\frac{392}{3\times 2} = \frac{392}{6} = 65.4$ g./l. In order to contain as much sulphate (SO_4) as a solution made from 2.5 g./l. of H_2SO_4, the solution of chromium sulphate must also be 0.05 *N*. Hence $0.05 \times 65.4 = 3.3$ g./l. of chromium sulphate must be used, *i.e.*, about 30 per cent more than of sulphuric acid. As however the chromium sulphate as purchased is seldom pure it is much easier to obtain the desired amount of sulphate by adding sulphuric acid.

Other additions such as hydrofluoric acid and boric acid have been suggested, but there are no published data showing the exact benefits derived from them. As each of these substances is difficult to determine analytically, it is preferable to employ the simpler solutions containing only the sulphate unless decided advantages can be gained by such additions.

A bath prepared from only chromic acid and sulphuric acid does not retain that composition during operation. At the cathode some of the chromium present in chromic acid, with a valence of six, is reduced to a valence of three, *i.e.*, to "trivalent chromium." Only part of this in turn is oxidized at the anode to chromic acid, and in consequence a used bath always contains some trivalent chromium. That which is first formed combines with the sulphuric acid to form chromium sulphate, $Cr_2(SO_4)_3$. Any excess of trivalent chromium is then present in compounds of somewhat indefinite composition, known as "chromium chromate," which may, according to different authors, be present either in true solution or in colloidal solution. There has been much discussion of the condition and effects of chromium chromate in plating solutions, but the subject is not yet clear. All that can be safely said is that when present in considerable amount, it decreases the conductivity of the solution, decreases the plating range for bright deposits, and slightly increases the throwing power. It is generally admitted that an excess should be avoided.

If for any reason the content of trivalent chromium has become excessive, its concentration may be decreased by operat-

ing the bath with a cathode in a porous cup, as proposed by H. S. Lukens.[1] Thus for example, when the bath is not in use, one or more porous clay pots or cups may be suspended in it. In each is placed a small iron cathode, and the cup is filled with the plating solution. Current is passed from the surrounding lead anodes, *e.g.*, over night. Under these conditions, much of the trivalent chromium in the tank solution, *i.e.*, the portion in contact with the anodes, will be oxidized to chromic acid. The solution in the cup will acquire a relatively high concentration of trivalent chromium, and may even form a precipitate of chromium chromate. At intervals this solution in the cup should be thrown away and replaced with a fresh portion of the bath.

It is claimed by some that small amounts of iron, introduced for example as "iron chromate," are beneficial. Recent results have shown that small amounts of iron have no measurable effect. It is generally admitted that an excess of iron is detrimental. Recently it was found[2] that iron, when present in relatively large concentrations, does not change the relation between current density and cathode efficiency, but it does increase the resistivity and reduce the range within which bright deposits are produced. Like trivalent chromium it slightly increases the throwing power when present in high concentrations.

One advantage of the solution prepared from chromic acid and sulphuric acid, is that each of the constituents is readily obtainable in a high state of purity. Chemically pure sulphuric acid usually contains about 98 per cent H_2SO_4 and can be readily weighed or measured. In the latter case it should be recalled that its specific gravity is about 1.84. Therefore to estimate the volume in cubic centimeters divide the weight in grams by 1.84. Suppose that a 100 l. bath is to contain 2.5 g./l. of H_2SO_4. Then it will require 250 g., which equals $250/1.84 = 136$ c.c. Similarly, 1 fluid ounce of water weighs about 1 avoirdupois ounce, and a fluid ounce of sulphuric acid weighs about 1.84 avoirdupois ounces. If then a 100 gal. bath is to be made up with 0.33 oz./gal. of sulphuric acid, this will require $100 \times 0.33 = 33$ avoirdupois ounces. This will have a volume of $33/1.84 = 18$ fluid ounces or $1\frac{1}{8}$ pints.

[1] *Trans. Am. Electrochem. Soc.*, vol. 53, p. 491, 1928.

[2] Schneidewind, R., Urban, S. F., and Adams, R. C., Jr., *Trans. Am. Electrochem. Soc.*, vol. 53, p. 499, 1928.

The chromic acid used until recently for chromium plating generally contained at least 98 per cent of CrO_3 and about 0.5 per cent of SO_4; together with small amounts of akali salts and insoluble matter. Such material is entirely satisfactory for preparing new baths, provided the content of SO_4 is known, so that a proper allowance may be made for it in adding the sulphuric acid. If however, as is now possible, material containing not more than 0.2 per cent SO_4 can be obtained, it is preferable, because then its sulphate content can be practically neglected in preparing the bath.

As chromium plating is conducted with insoluble anodes, it is necessary at intervals to replace the chromic acid that is actually deposited as metallic chromium, as well as that which is removed by the spray and drag-out. The solution thus removed contains not only chromic acid but also sulphate which must be replaced. The ratio of chromic acid and sulphate required to replenish the bath is not the same as that used originally. Suppose for illustration that the loss of chromic acid by spray and drag-out is just equal to that actually used in the chromium deposition. Then it would be necessary to add chromic acid and sulfuric acid in the ratio of 200 to 1 instead of the original 100 to 1. For this purpose chromic acid containing 0.5 per cent SO_4 would be very satisfactory, as no additional sulphuric acid would be needed. But the ratio of the losses is likely to change with different operating conditions, and the sulfate content of different lots of chromic acid, even from the same firm, may not be constant. In one case a plater who had successfully maintained a chromium bath for a year by additions of chromic acid encountered difficulty when a new supply was purchased. Analyses showed that, for his method of operation, the new chromic acid was too pure! It is therefore much more satisfactory to determine by occasional analyses, the amounts of chromic acid and sulphuric acid actually required, and to add the necessary quantities of the pure materials. There is no difficulty in purchasing chromic acid on a specification requiring not less than 98 per cent of CrO_3 and not more than 0.2 per cent of SO_4, which will meet all present requirements.

If for any reason the content of sulphate in a bath is too high, it can be reduced[1] by adding the required amount of freshly

[1] This suggestion was made by Graham A. K. and quoted by Lukens H. S. (*Trans. Am. Electrochem. Soc.*, vol. 53, p. 496, 1928).

precipitated barium chromate ($BaCrO_4$), or barium carbonate, ($BaCO_3$) which at once produces barium chromate in the solution. The reaction by which barium sulphate is precipitated is relatively slow on account of the slight solubility of the barium chromate. The solution should therefore be well agitated for several hours and then allowed to settle. It is advisable to filter the solution or drain it off and remove the precipitate. If it is suspected that the sulphate content is too high, but no chemical analyses are available, it may be most convenient to add a slight excess of barium chromate and thus remove all the sulphate. The precipitate is allowed to settle, and the solution is removed by decantation. The desired amount of sulphuric acid is then added.

2. ANODES FOR CHROMIUM PLATING

As previously noted, insoluble anodes are usually employed in chromic acid baths. Schwartz[1] and others have shown that chromium anodes can be used, but as they are more expensive than chromic acid, and as they tend to produce an excessive concentration of chromium chromate, they are not advantageous. Lead or steel anodes are generally employed. Haring and Barrows showed that the lead anodes are preferable to steel because on lead the trivalent chromium is more completely oxidized to chromic acid than upon steel. Hence there is less tendency for the accumulation of chromium chromate with lead than with steel anodes. In general, it is desirable to have the anode area as large as possible, as with a low anode current density the oxidation is more complete. O. P. Watts[2] also came to the conclusion that lead anodes are preferable to iron or steel anodes.

R. Schneidewind and S. F. Urban[3] have shown that the equilibrium concentration of trivalent chromium is lower with lead than with iron anodes. They found that with steel anodes the iron dissolves in the bath more rapidly at low than at high current densities. E. M. Baker and E. E. Pettibone[4] showed that pure electrolytic iron is least attacked as anode in the chromic acid bath, and that as the carbon content of the iron or steel is increased, the rate of solution is increased. If therefore or any reason iron or steel anodes are used, they should be as

[1] *Trans. Am. Electrochem. Soc.*, vol. 44, p. 451, 1923.
[2] *Trans. Am. Electrochem. Soc.*, vol. 52, p. 177, 1927.
[3] *Trans. Am. Electrochem. Soc.*, vol. 53, p. 457, 1928.
[4] *Trans. Am. Electrochem. Soc.*, vol. 54, p. 331, 1928.

nearly pure iron as practicable, *e.g.*, a low carbon steel. No satisfactory method of removing iron from the baths has thus far been published. Hence when the iron content of the bath reaches an objectionable figure, a part at least of the bath must be discarded and replaced with fresh solution.

Although lead anodes are almost universally employed in chromium plating, difficulties are sometimes experienced with the accumulation upon them of an adherent coating of lead chromate and lead peroxide, which increases the resistance to such an extent as to materially decrease the current density unless the voltage is raised. In some plants it is necessary to clean the anodes at intervals, and even as often as daily. The coating may be removed by dipping the anodes in a saturated solution of sodium chloride containing a small amount of hydrochloric acid, or in a sodium hydroxide solution. In other plants, or under other conditions, no such trouble is encountered and lead anodes are not removed from the solutions for months. In the latter procedure it may be necessary to apply a higher voltage at the beginning of the working day, which is usually done by inserting a "dummy cathode" and using the current also to heat the solution to the desired temperature. Removal of the anodes when not in use over night decreases their attack. No conclusive explanation of these differences in the behavior of lead anodes has been offered; and it still remains to be determined whether they are due to differences in the composition of the solution, in the purity of the lead, or in the anode current density. It has been found that an alloy of lead with 6 per cent of antimony is more satisfactory than pure lead. The use of a thick lead anode reduces the local heating by the passage of current and is said to decrease the tendency to form an adherent coating.

3. OPERATING CONDITIONS

As explained in Chapter VII, the structure of an electrodeposit and hence its properties such as color, luster, hardness, ductility and porosity, may be appreciably affected by the conditions under which it is deposited, such as the bath composition, temperature and current density. Chromium is no exception, and many of the factors in chromium deposition might be predicted upon general principles. The effects of certain variables such as temperature and current density are however so

pronounced with chromium, that in order to produce uniformly satisfactory deposits for any given purpose, it is necessary to exercise much closer control over the operating conditions than in any other commercial plating bath. While this situation has brought many new problems to the plater, and has somewhat retarded the development of chromium plating, it has served a useful purpose in emphasizing the desirability of similar control in other plating processes, where the effects may be less striking but still important.

The most valuable properties of electrodeposited chromium are its extreme hardness and its resistance to tarnish (p. 125). These properties lead respectively to its use for wear resistance and for appearance. For the latter purpose it is generally desirable that the chromium plated articles have a high luster. Owing to the hardness of the chromium it is difficult to buff a dull deposit, hence it is especially advantageous to produce bright deposits which require little or no buffing.

Even when the underlying metal is bright it is not possible to produce bright deposits except within certain limits of temperature and current density, which must be defined not only for each composition of solution, but also for each metal upon which the chromium is to be plated. In addition it is desirable to select the conditions which will yield as high a cathode efficiency and throwing power as possible, as at best these are very low. It is obvious therefore that it is not possible to specify a solution and operating conditions which will meet all conceivable requirements. It is possible however to define certain "plating ranges," and to point out the directions in which a given improvement is most probable.

According to their appearance, chromium deposits may be divided roughly into four classes, between which however there is no sharp dividing line. In the order of increasing cathode efficiency, these are (*a*) milky, (*b*) bright, (*c*) frosty and (*d*) burnt. For a given solution the current densities required respectively to produce these deposits depend upon the temperature. In general as the temperature is increased, the current density must also be increased in order to produce a bright deposit. Frosty and burnt deposits are usually an evidence of (*a*) too high a current density for the prevailing temperature or (*b*) of too low a temperature for the current density employed.

Schneidewind, Urban and Adams[1] have shown that over a wide range of temperatures and current densities bright deposits are produced when the cathode efficiency is from 5 to 20 per cent with an optimum of about 13 per cent. Thus in one experiment they produced with 13 per cent efficiency a bright deposit about 2.5 mm (0.10 in.) thick in 35 hr. by using a current density of 95 amp./dm.^{2} (850 amp./sq. ft.) at 85°C. (185°F.). It is very difficult to produce from the usual solutions bright deposits at

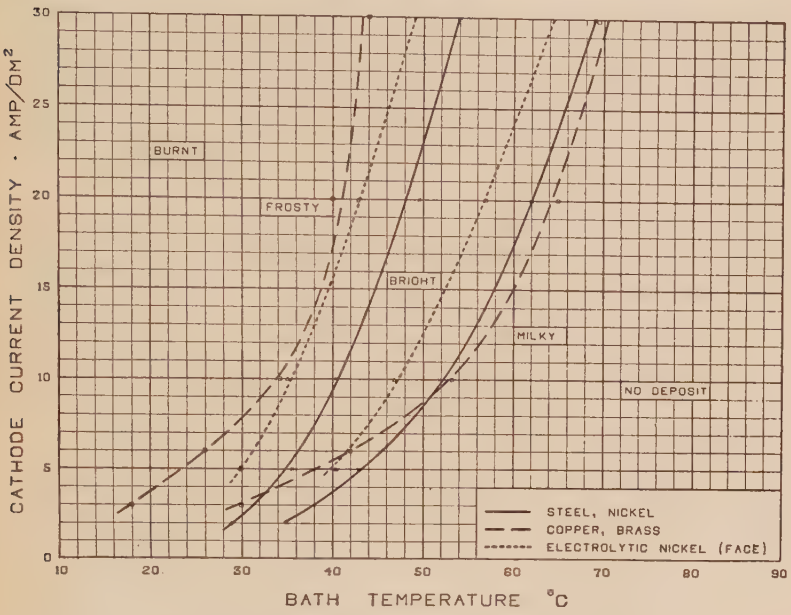


Fig. 31.—Operating Diagrams on Different Metals for a Bath 2.5 *M* in CrO_3 and 0.05 *N* in SO_4.

temperatures below 30°C. (86°F.), or below 4 amp./dm.^{2} (37 amp./sq. ft.).

In Fig. 31, derived from Haring and Barrows, are shown typical curves for the plating ranges of a simple bath upon different metals. In general the range is greater at high than at low temperatures and current densities. Thus on copper or brass at 50°C. (122°F.) and an average current density of 25 amp./dm.^{2} (230 amp./sq. ft.) it is possible to produce a bright deposit all over an article of such a shape that the maximum current density is 5 times the minimum. At 35°C. (95°F.) and an average of 11

[1] *Trans. Am. Electrochem. Soc.*, vol. 53, p. 499, 1928.

pam./dm.^{2} (100 amp./sq. ft.) however, bright deposits can be produced only when the ratio of maximum to minimum current density is not more than 2.6. Schneidewind in his monograph (No. 11) on chromium plating, concluded that a CrO_3 concentration of about 300 g./l. yields the widest plating range (at 25°C.). Inspection of his data shows that with 300 g./l. CrO_3, the range in current densities for bright deposits is largest numerically, but that with 250 g./l. CrO_3 the *ratio* of the plating range is greatest. For most purposes it is this ratio of the minimum and maximum current densities, rather than their difference, which determines the utility of the solution for plating an irregular article with a bright deposit. According to his data therefore a concentration of about 250 g./l. of CrO_3 is preferable. Similarly his results show that the widest plating ratio is obtained when CrO_3/SO_4 = about 150 : 1.

To some extent at least, the character of the entire chromium deposit is determined by that of the coating produced during the first few seconds. If, *e.g.*, the initial current density is excessive on some points and burning occurs there, the subsequent deposit will be dull or burnt at those points. In some plants this difficulty is overcome by plating for a brief period at a low average current density. This produces a bright or even milky deposit on the exposed portions, and little or no deposit on the recessed parts. The current density can then be raised to a sufficiently high value to plate in the recesses without burning the projections. Such expedients may be rather troublesome; but they permit production plating of articles that would otherwise be very difficult to plate with a uniformly bright coating.

The throwing power in chromium plating is notoriously poor; and, in spite of the many investigations conducted in recent years, no conclusive evidence of any significant improvement in throwing power has been published. The low throwing power seems to be inseparably connected with this type of bath. While the total cathode polarization is high, it does not change appreciably with the current density within the range of bright deposits. The conductivity of the solution is good, but at the high current densities required, the total voltage drop (IR) through the solution is relatively great. This fact still further decreases the effect of the small change in polarization. The principal cause of the poor throwing power however is the fact that the cathode efficiency, never very high, decreases rapidly

at the low current densities that exist in depressions; consequently the throwing power is negative. Suppose that a brass article of such a shape is to be plated, that the maximum current density is five times the minimum. As previously noted, a bright deposit may be produced all over such an article at 50°C. (122°F.) if the average current density is 25 amp./dm.^{2} (230 amp./sq. ft.). Under such conditions the minimum current density might be 8 amp./dm.^{2} (65 amp./sq. ft.) and the maximum 40 amp./dm.^{2} (370 amp./sq. ft.). But at the lower current density the cathode efficiency will be only about 9 per cent and at the higher current density about 20 per cent. Therefore the deposit will be over 10 times as thick on the near as on the far plate, or the throwing power will be about −100 per cent.

In a report made in July, 1929, to the American Electroplaters' Society by H. L. Farber[1] on a study of throwing power at the Bureau of Standards, the following conclusions were reached. These are based on experiments in a throwing power box with a primary ratio of 2:1.

(1) The throwing power is determined almost entirely by the cathode efficiencies, and can be improved by making these efficiencies more nearly equal at the maximum and minimum current densities used.

(2) At a given current density an increase in temperature reduces the throwing power.

(3) At a given temperature, an increase in current density improves the throwing power.

(4) Good throwing power and bright deposits can be obtained more readily at high temperatures and current densities than at low. A higher voltage is required however.

(5) Dilute solutions of chromic acid give better throwing power for a given current density. As however their resistance is greater, a higher voltage is needed. For a given voltage (*e.g.*, 5 volts at the tank), better throwing power is obtained in the more concentrated solution.

(6) A low content of sulphate, *e.g.*, $CrO_3/SO_4 = 200$ gives slightly better throwing power than a ratio of 100, and much better than a ratio of 50.

(7) Sodium dichromate, added in large amounts to a solution with a sulphate ratio of 100, slightly improves the throwing

[1] Bureau of Standards, *Journal of Research* vol. 4, p. 27, 1930.

power, probably by changing the sulphate ratio. If the latter is 200, the addition of sodium dichromate is detrimental.

(8) Boric acid has no appreciable effect on the throwing power.

(9) Small concentrations of trivalent chromium have no effect on throwing power. High concentrations increase the throwing power, making it equal to that of a more dilute solution. As the resistance of the bath is thereby increased and the plating range decreased, trivalent chromium is not advantageous.

(10) Iron has practically the same effects on throwing power as trivalent chromium, but a greater detrimental effect on the resistivity and plating range.

(11) Polished metal surfaces yield better throwing power than rough surfaces.

(12) The throwing power is slightly better on steel and brass than on copper and nickel.

In the experiments of Farber the best throwing power (−13 per cent) with bright deposits, was obtained in a solution containing 250 g./l. (33 oz./gal.) of CrO_3 and 1.25 g./l. (0.17 oz./gal.) of SO_4, at a temperature of 55°C. (131°F.) and an average current density of 35 amp./dm.^{2} (325 amp./sq. ft.). This required in the box, 6.4 volts. Such conditions are suggested for use when a voltage above 6 is available, and when the best attainable throwing power is desired.

When the voltage is limited, and, *e.g.*, only 5 volts is available at the tank, a fair throwing power (about −60 per cent) can be obtained with 400 g./l. (53 oz./gal.) of CrO_3 and 2 g./l. (0.27 oz./gal.) of SO_4, at a temperature of 45°C. (113°F.) and an average current density of 15 amp./dm.^{2} (140 amp./sq. ft.).

In the latter solution, at a temperature of 35°C. (95°F.) and an average current density of 7.5 amp./dm.^{2} (70 amp. /sq. ft.), a throwing power of about −60 per cent is also obtained. This is usually satisfactory if the articles are not of very irregular shape, or are favorably placed in the tank.

The above conclusions were confirmed by Farber by tests with bent cathodes, such as were used by O. J. Sizelove[1] and by W. L. Pinner and E. M. Baker.[2] Farber found that on a copper cathode, bent at a right angle, and placed in the throwing power box so that the ratio of distances from the anode to the far and near

[1] *Monthly Review, Am. Electroplaters' Society*, vol. 16, No. 4, April 1929.
[2] *Trans. Am. Electrochem. Soc.*, vol. 55, p. 315, 1929.

points was also 2:1, the covering power was practically parallel to the throwing power as previously measured.

As noted on p. 116, the successful application of chromium plating to articles of irregular shape depends largely upon ingenuity in so racking the work as to obtain as nearly a uniform current density as possible over the cathode surface. If in this way the ratio of the maximum to minimum current density is made less than 2:1, good results are usually obtainable.

Various methods are used in introducing the cathodes into the solution. Brass and copper are so readily attacked by chromic acid that it is necessary to have them connected with the cathode as soon as they are introduced, and a sufficient voltage applied to cause chromium deposition at once over the whole surface. Steel and iron may be hung in the solution without appreciable attack, though it is sometimes preferable to have them connected to the cathode in advance. By making iron or steel anodic in the solution for 30 to 60 seconds an improvement in distribution has sometimes been obtained. This may be caused by the oxidizing effect upon impurities such as carbon on the surface. It has also been attributed to the fact that the anodic action renders the surface of the steel passive.

The choice of the operating conditions depends upon the purpose for which the chromium deposit is to be used. For very thin coatings such as are applied over nickel on exposed parts of automobiles, the most essential requirement is to produce a bright deposit. Even here, however, it is desirable to produce as nearly impervious coatings as possible, in order to secure the maximum protective value. E. M. Baker and W. L. Pinner[1] came to the conclusion that, when applied over a composite layer of nickel, copper and nickel on steel, relatively thin chromium deposits exert better protection than thicker ones. They found that under their usual conditions of deposition, chromium coatings with a thickness of from 0.0003 to 0.0006 mm. (0.000013 to 0.000025 in.) were most satisfactory. In a more recent investigation,[2] tests were made of the porosity of chromium coatings upon nickel. These experiments showed that in a 2.5 *M* bath (250 g./l. or 33 oz./gal. CrO_3) at 55°C. (131°F.) the least porous coatings had a thickness of about 0.0009 mm.

[1] *Soc. of Automotive Eng.*, vol. 22, p. 331, 1928.

[2] Baker, E. M., and Rente, A. M., *Trans. Am. Electrochem. Soc.*, vol. 54, p. 337, 1928.

(0.00004 in.). A still lower porosity was observed in thicker deposits produced in more concentrated baths or at higher temperatures. Baker confirmed the previous observations of L. E. and L. F. Grant,[1] L. Wright,[2] and others, that the porosity of chromium deposits is due principally to fine cracks in the surface. Such cracks are more pronounced in the hardest chromium deposits. This fact suggests the desirability of selecting for protective coatings, conditions which may produce a somewhat softer, but more nearly impervious deposit; and for wear resistance those that produce the hardest deposits that will adhere under the required conditions of service.

Although it is not possible to specify the most favorable operating conditions for a given purpose, helpful suggestions may be obtained from the following table derived from Haring and Barrows. In this table the term "electrolytic nickel face"

OPERATING DATA FOR A BATH 2.5 *M* (250 G./L. OR 33 OZ./GAL.) IN CrO_3 AND 0.05 *N* (2.5 G./L. OR 0.33 OZ./GAL.) IN SO_4

Cathode	Bath temperature		Ratio of limiting current densities	Optimum average current density		Approximate average efficiency. Per cent	Time required to deposit average of 0.005 mm. or 0.0002 in. Minutes
	°C.	°F.		amp./sq. ft.	amp./dm.²		
Steel or nickel...	35	95	2.5	35	3.5	7	255
	40	104	2.5	60	6.5	10	96
	45	113	2.6	100	10.5	12	50
	50	122	2.7	150	16.0	13	30
	55	131	2.6	200	21.5	14	21
Copper or brass	35	95	2.6	70	7.5	11	76
	40	104	3.1	100	11.0	13	44
	45	113	4.7	190	20.0	15	21
	50	122	5.0	235	25.0	17	15
Electrolytic nickel face	35	95	3.2	55	6.0	9	116
	40	104	3.2	100	10.5	12	50
	45	113	2.7	145	15.5	14	29
	50	122	2.4	205	22.0	15	19

[1] *Trans. Am. Electrochem. Soc.*, vol. 53, p. 509, 1928.

[2] *J. Electroplaters and Depositors Tech. Soc.*, vol. 3, p. 25, 1928.

refers to the initial surface of nickel deposited upon and separated from a metal mold, as in the reproduction of printing plates. The simplest explanation of the greater difficulty of depositing chromium upon such a surface, is that it is much finer grained and may therefore have a different hydrogen overvoltage than the side of the nickel last deposited, *e.g.*, upon the outside of a plated surface. This explanation does not however account for the fact that it is much harder (and sometimes virtually impossible) to deposit chromium upon a wax molded nickel electrotype than on a lead molded nickel electrotype. H. S. Lukens[1] concluded that this behavior was due to passivity of the nickel deposited on graphited wax. Other observations indicate that it may be due to a very persistent film of wax or graphite "burned" into the nickel surface during the backing up with type metal. Thus far no entirely satisfactory explanation or remedy has been found. In some plants a very thin coating of copper is applied to the face of the nickel, after which chromium can be readily deposited on the copper. In others, a very vigorous polishing of the nickel surface puts it into a satisfactory condition for chromium plating.

At the present time there is no general agreement regarding the best procedure for chromium plating upon brass, and especially as to whether it should be applied directly or over a coating of nickel. Experience shows that thin chromium coatings are not impervious. Hence it would appear desirable to precede the chromium with nickel just as is commonly done in plating steel. Unfortunately it is found that even with the greatest of care in the preparation and in the nickel plating, there is a tendency for the subsequent chromium plating process to cause peeling of the nickel. This tendency increases as the thickness of the chromium is increased. For this reason it is customary to apply over the nickel, a thickness of only about 0.0005 mm. (0.00002 in.); as compared with up to 10 times that thickness when chromium is applied directly to the brass. No conclusive data are available as to the relative serviceability of these two types of coating, *e.g.*, upon plumbing fixtures, where resistance to both tarnish and abrasion is important. The present practice in America tends toward direct chromium plating on cast brass. On wrought or drawn brass, the application of nickel reduces the tendency of the chromium to flake off, especially when

[1] *Trans. Am. Electrochem. Soc.*, vol. 53, p. 490, 1928.

exposed to corrosive conditions. It has been suggested that this flaking of chromium from drawn brass may be associated with excessive strains in the brass,such as cause "season cracking." It has also been observed that this flaking is more common on a "high" (zinc) brass than a low. Thus it is claimed that less trouble is experienced with flaking of chromium from an 80 copper-20 zinc brass than from a 65-35 brass. In general, cracking of chromium is more likely to occur at points with an excessive current density. A thin copper deposit on brass increases the adherence of the chromium. The tendency of the chromium to cause peeling of nickel previously deposited upon brass, is governed largely by the adherence of the nickel (p. 133) and partly by the brittleness. Whenever it is feasible to buff the nickel before applying chromium, it is desirable to employ those conditions for nickel deposition which produce relatively soft, ductile nickel; such as a low current density, high nickel content, high pH, and high temperature. When however a bright nickel deposit is essential, these factors should be varied in the opposite direction, but only as much as necessary for the requisite brightness. The deposition of a thin coat of acid-copper on the brass before the nickel increases the adherence of the latter.

Although chromium has been successfully applied to many other metals, very few details of operation have been published. It is possible to deposit it directly upon zinc and zinc-base die castings, but a high current density must be used to prevent attack of the zinc, and the deposits are likely to be dull or burnt. Such deposits develop cracks and have little protective value. It is therefore common practice to plate with nickel before the chromium plating, both on sheet zinc and on die-cast automobile hardware. In this process difficulty may also be experienced with peeling of the nickel unless special precautions are taken both in cleaning the zinc before nickel plating, and in producing as ductile nickel as practicable. A dip in dilute acetic acid or hydrofluoric acid before nickel plating improves the adherence. Unfortunately the conditions that are most favorable for plating nickel on zinc (p. 254) in order to prevent deposition by immersion and dark streaks, all involve increased cathode polarization. This in turn tends to form bright but hard nickel. It is necessary therefore in plating nickel on zinc preparatory to chromium plating, to keep the polarization as low as possible and

yet completely plate the zinc. For this purpose a lower concentration of sodium citrate or of sulphate, and a slightly higher temperature and pH, and a lower current density should be used than are customary when nickel only is to be applied to the zinc (p. 254).

Not much success has been reported upon plating chromium directly upon aluminum or its alloys. As noted on p. 257, successful adherence of nickel upon aluminum depends most largely upon producing a roughening of the surface, *e.g.*, by selective etching. Similar methods of etching have proved satisfactory as a preparation for direct chromium plating. At present, however, most of the chromium plated aluminum goods have received a preliminary coating of nickel. Unfortunately, just as with brass, it is difficult to apply a thick coating of chromium over nickel on aluminum. The coating is therefore chiefly useful for appearance and not for extreme wear resistance.

Ventilation.—It is essential that good ventilation be provided for all chromium plating tanks, in order to remove the spray of chromic acid that is carried into the air by the oxygen evolved from the insoluble anodes, and by the hydrogen from the cathodes. It has long been known that chromic acid and chromates are very injurious to the nasal tissues, and may even perforate the nasal septum. It has recently been shown[1] that exposure for a few weeks to a concentration of CrO_3 as low as 1 mg. of CrO_3 in 10 cubic meters, or 1/60 gr. in 350 cu. ft. (which is about the volume of air breathed by a worker in 8 hr.) is sufficient to cause such injuries. The most effective means of completely removing it from the air breathed by the operators, is by cross ventilation into a slot or duct along one side of the tank. If the air in the slot has a velocity of 1,500 to 2,000 ft. per minute or 500 to 650 meters per minute, the ventilation will be effective for a tank not more than 18 to 20 in. (45 to 50 cm.) wide. For wider tanks, ducts should be provided on both sides. It is also advisable to keep the level of the plating solution at least 8 in. (20 cm.) below the top of the tank. If for any reason the ventilation is not adequate, injury to the nose can be prevented or retarded by occasional application of vaseline.

Chromic acid produces severe sores or "chrome holes" wherever it comes in contact with abraded skin. If feasible, rubber

[1] Bloomfield, J. J. and Blum, W., Health hazards in chromium plating, *Public Health Reports*, vol. 43, p. 2330, 1928.

gloves, aprons and boots should be worn. Otherwise the hands should be frequently washed, and vaseline or lanolin applied to all open cuts or sores. If chromic acid has attacked them, a reducing agent such as sodium thiosulphate (hypo) or ammonium polysulphide should be applied, followed by an ointment. With reasonable care, no serious health hazard will exist in chromium plating.

4. SUGGESTED FORMULAS

As previously indicated, many at least of the formulas proposed for chromium plating give practically identical results. The simplest formula for a bath for general purposes is as follows:

			g./l.	oz./gal.
(1)	Chromic acid, CrO_3	2.5 *M*	250	33
	Sulphuric acid, H_2SO_4	0.025 *N*	1.25	0.17
		to	to	to
		0.05 *N*	2.5	0.33

Temperature 45° to 55°C. (113° to 131°F.), average current density 10 to 30 amp./dm.^{2} (93 to 280 amp./sq. ft.)

The use of high temperatures and consequently high current densities, often requires the application of 8 volts or more. In order to operate at 6 volts, *i.e.*, with the regular plating generators, it is desirable to use a lower temperature and current density, and to have a very well conducting solution. For this purpose a bath and conditions such as the following are desirable:

		N	g./l.	oz./gal.
(2)	Chromic acid	4.0	400	53
	Sulphuric acid	0.04	2	0.27

Temperature 30° to 35°C. (86° to 95°F.), average current density 4 to 8 amp./dm.^{2} (37 to 75 amp./sq. ft.)

Other sulphates, such as of chromium, sodium, potassium and magnesium, may be substituted in equivalent amounts for the sulphuric acid. In the last column of the table on page 307 are given the concentrations of these sulphates equivalent to 0.05 *N* sulphuric acid, *i.e.*, the concentrations to be used in a bath containing 250 g./l. (33 oz./gal.) of chromic acid, and 2.5 g./l. (0.33 oz./gal.) of sulphate (SO_4).

EQUIVALENT WEIGHTS OF VARIOUS SULPHATES

Name	Formula	Molecular weight	Equivalent weight	Concentration 0.05 *N*	
				g./l.	oz./gal.
Sulphuric acid.....	H_2SO_4	98	49	2.5	0.33
Sodium sulphate[1].....	Na_2SO_4	142	71	3.5	0.47
Sodium sulphate[2].....	$Na_2SO_4.10H_2O$	322	161	8.0	1.07
Potassium sulphate.....	K_2SO_4	174	87	4.4	0.59
Magnesium sulphate....	$MgSO_4.7H_2O$	246	123	6.1	0.81
Chromic sulphate[1].....	$Cr_2(SO_4)_3$	392	65	3.3	0.44

[1] Anhydrous.

[2] Crystals containing water.

5. METHODS OF ANALYSIS

The most important constituents of a chromium bath are chromic acid (CrO_3) and sulphate (SO_4). The exact concentrations of these are not so important as the ratio between them, which should be not less than 100 to 1, and for the best throwing power should be about 200 to 1. The approximate concentration of the chromic acid may be estimated from the density, as measured with a hydrometer. In Table 14 in the Appendix will be found the concentrations of *pure* chromic acid corresponding to different densities. As the content of sulfate in the bath is small, it has very little effect upon the density. As, however, the latter is also affected by trivalent chromium that may be present, it is not an accurate measure of the chromic acid content. The density is especially useful to detect large changes in concentration such as may occur through leaks or overflows.

The customary method of determining sulfate in solutions involves precipitation with barium chloride and weighing of the resultant barium sulphate. This method requires regular laboratory facilities including a balance, and is not suitable for rapid works control by the plater. Efforts have been made by various investigators to adapt simple methods to the approximate determination of sulphate in chromium baths. Among the most promising are (1) that used by Kocour, depending upon measuring the volume of the barium sulphate after centrifuging the solution to cause the precipitate to settle into a small graduated portion of the tube; and (2) those of Stout and Petchaft[1] and of Willard

[1] *Trans. Am. Electrochem. Soc.*, vol. 56, preprint, 1929.

and Schneidewind[1] *i.e.* the measurement of the turbidity produced by a strontium or barium sulphate precipitate. Recently[2] a simple, rapid test for determining the optimum content of sulphate by plating upon a bent cathode, was described by Baker and Pinner.

Other determinations that may be required for the control of the solution are (*a*) trivalent chromium and (*b*) iron. Both of these involve considerable laboratory experience. The trivalent chromium is usually determined indirectly, *i.e.*, by the difference between the total chromium and the hexavalent chromium (*i.e.*, the CrO_3), although it may be determined directly.

The volumetric methods for the determination of hexavalent chromium (Cr^{VI}) depend upon the fact that it is a strong oxidizing agent, and can be reduced to trivalent chromium (Cr^{III}) by a reducing agent such as ferrous sulphate ($FeSO_4$). The reaction involved is as follows:

$$2Cr^{+VI}O_3 + 6Fe^{+II}SO_4 + 6H_2SO_4 = Cr_2^{+III}(SO_4)_3 + 3Fe_2^{+III}(SO_4)_3 + 6H_2O$$

From this equation it is evident that three molecules of ferrous sulphate are required to reduce each molecule of chromic acid. From the amount of ferrous sulphate consumed, the concentration of the chromic acid can be computed. In principle therefore all that is necessary is to add a ferrous sulphate solution of known strength to the chromic acid (containing an excess of sulphuric acid) until the chromic acid is entirely reduced. The two methods most commonly used differ chiefly in the means of determining the end point.

In the electrometric method advantage is taken of the fact (p. 48) that the potential of a platinum wire immersed in a solution, is altered greatly when the solution changes from an oxidizing to a reducing condition. The ferrous sulphate is therefore added to the chromic acid until the potential of the platinum wire (measured with respect to a calomel electrode) undergoes a large change, as shown by the deflection of a galvanometer. This marks the end point.

The chemical method depends upon adding an excess of ferrous sulphate to the chromic acid and titrating the excess with a standard permanganate solution. The same reagents

[1] *Trans. Am. Electrochem. Soc.*, vol. 56, preprint, 1929.

[2] *Trans. Am. Electrochem. Soc.*, vol. 55, p. 315, 1929

are required in the two methods, except that no permanganate is used in the electrometric titration. The latter is more convenient and rapid if such tests are to be made regularly. The chemical method is better for occasional titrations, as no special equipment is required. The chemical method will be described in detail, as it can readily be adapted to the electrometric procedure by anyone accustomed to the latter.

It is also possible to determine the hexavalent chromium by its reaction with potassium iodide to liberate iodine, which is then titrated with sodium thiosulfate, using starch as an indicator. This method, which has been used to a considerable extent for analyzing chromium plating solutions, is reliable for nearly pure solutions, but not for those containing much iron. This is because ferric iron also liberates iodine, so that the result of the titration includes both hexavalent chromium and iron. When iron tanks or iron anodes are used, the solution may in time contain 15 g./l. or more of iron, which may introduce a serious error in the chromium determination. For this reason the method employing the ferrous sulphate reduction is preferable.

As explained on p. 27, a normal solution is one containing in each liter one equivalent weight in grams of the substance. It is necessary however to distinguish between a solution that is normal with respect to neutralization, and one that is normal with respect to oxidation and reduction. Thus, considered as an acid, chromic acid, which may be written H_2CrO_4, is dibasic, and hence a normal solution contains $118/2 = 59$ g./l. of H_2CrO_4 or $100/2 = 50$ g./l. of CrO_3. But when CrO_3 acts as an oxidizing agent, each atom of chromium loses three valences, *i.e.*, it changes from Cr^{+VI} to Cr^{+III}, *e.g.* from CrO_3 to Cr_2O_3. Hence a normal solution of chromic acid, as an oxidizing agent, contains $100/3 = 33.3$ g./l. of CrO_3. To avoid confusing the latter normalities with those computed from the ordinary neutralizing or replacing power, *the oxidizing-reducing normalities will be designated as* N_0. Thus a 0.1 N_0 solution of chromic acid contains $1/10 \times 100/3 = 3.3$ g./l. of CrO_3.

(a) **Sulphate Determination.**—Ten cubic centimeters of the bath sample is diluted to about 125 c.c., 10 c.c. of concentrated hydrochloric acid[1] added, and then 10 c.c. of 95 per cent ethyl

[1] The amount of hydrochloric acid to be added should be sufficient to combine with the chromium present and to leave an excess equivalent to about 4 c.c. of concentrated hydrochloric acid. From the equation

alcohol. The alcohol reduces the chromic acid to chromium chloride ($CrCl_3$), at the same time forming aldehyde (CH_3CHO). The solution is boiled carefully to expel the aldehyde and the excess of alcohol. The solution is diluted to about 200 c.c., 10 c.c. of a barium chloride solution (containing about 50 g./l. of $BaCl_2.2H_2O$) is added slowly, and the boiling is continued for a few minutes. After standing over night the solution is filtered and the precipitate of barium sulphate ($BaSO_4$) is washed and ignited and weighed. As the equivalent weight of $BaSO_4$ is 233/2 = 116.7, the weight of $BaSO_4$ from 10 c.c. multiplied by 100 and divided by 116.7, gives the sulphate normality (N) of the solution.

Example.—If the precipitate of $BaSO_4$ from a 10 c.c. sample weighed 0.0632 g., the sulphate normality is equal to $\frac{0.0632}{116.7} \times 100 = \frac{6.32}{116.7} =$ 0.054 N. As the equivalent weight of sulphuric acid is 98/2 = 49 g./l., the sulphate in the solution corresponds to 0.054 × 49 = 2.65 g./l. = 0.35 oz./gal. of H_2SO_4, or to equivalent concentrations of other sulphates that may be present.

(b) Chromic Acid (Hexavalent chromium).—The following reagents are required:

(*a*) A tenth normal (0.1 N_0) *dichromate* solution is prepared from $K_2Cr_2O_7$ of known high purity, *e.g.*, that made by recrystallization, powdering and drying at 130°C. If exactly 4.90 g. is dissolved and diluted to one liter the solution is 0.1 N_0 in its oxidizing power, *i.e.* is equivalent to 0.1 N_0 CrO_3.

$2\,CrO_3 + 6HCl + 3C_2H_5OH = 2CrCl_3 + 6H_2O + 3C_2H_4O$ it may be shown that each 10 c.c. of molar (M) CrO_3, (*i.e.* 0.01 mol of CrO_3) requires 0.03 mol of HCl, or 1.1 g. HCl. As the concentrated hydrochloric acid (sp. gr. 1.20) is about 13 molar, it requires about 2.5 c.c. of concentrated hydrochloric acid to combine with each 10 c.c. of molar CrO_3. Thus for 10 c.c. of a bath that is 2.5 M in CrO_3, it is necessary to use 2.5 × 2.5 = 6.3 c.c. of concentrated hydrochloric acid, plus about 4 c.c. to furnish the necessary free hydrochloric acid, or about 10 c.c. of hydrochloric acid in all. If in another case the bath is 4 M, 10 c.c. will require 4 × 2.5 = 10 + 4 = 14 c.c. of hydrochloric acid. If too little hydrochloric acid is present the reduction may be incomplete and basic chromium compounds may be precipitated with the barium sulphate. If too much or too little acid is present, the precipitation of barium sulphate is incomplete. Willard and Schneidewind (*Trans. Am. Electrochem. Soc.*, vol. 56, preprint, 1929) found that the above method of determining sulphate is not very exact unless the solution stands at least 16 hr. before filtration. They recommend the addition of 7 c.c. of hydrochloric acid and 25 c.c. of glacial acetic acid. This permits filtration in 1 hr.

(*b*) A *ferrous ammonium sulphate* solution, approximately 0.1 N_0, containing about 40 g./l. of the salt, $FeSO_4.(NH_4)_2SO_4.6H_2O$ and 135 g./l. (or 75 c.c./l.) of concentrated sulphuric acid. The ferrous ammonium sulphate simply serves as a convenient source of pure ferrous sulphate, and the ammonium sulphate present in it has no effect upon the titration.

(*c*) An approximately tenth normal (0.1 N_0) permanganate solution, containing about 3.2 g./l. of $KMnO_4$.

As the ferrous sulphate solution slowly changes in strength (owing to oxidation) it is necessary to determine its relation to the permanganate and dichromate solutions each day that a chromic acid determination is made.

To determine the ratio between the $FeSO_4$ and $KMnO_4$ solutions, measure exactly 25.0 c.c. of $FeSO_4$ into a beaker, dilute to about 300 c.c., add 25 c.c. of concentrated H_2SO_4, cool and titrate with the $KMnO_4$ till a faint pink color persists for one minute.

To determine the ratio between the $FeSO_4$ and $K_2Cr_2O_7$ solutions, place 25.0 c.c. of the $K_2Cr_2O_7$ in a beaker and dilute to about 300 c.c. Then add exactly 50 c.c. of $FeSO_4$, (*i.e.* a considerable excess) and titrate the excess $FeSO_4$ with $KMnO_4$ to an end point which persists for one minute. The green color due to the trivalent chromium tends to mask the end point, which can however be readily detected after a little experience. (For very precise work, a small correction should be made for the volume of $KMnO_4$ required to produce the end point in the green solution. This may be determined by boiling the solution at the end of the above titration for ten minutes to destroy the slight excess of $KMnO_4$; cooling and again titrating with the $KMnO_4$.) The excess of ferrous sulphate, which is equivalent to the permanganate used in the back titration, is subtracted from the total ferrous sulphate added. The balance then represents the volume of ferrous sulphate required to reduce the $K_2Cr_2O_7$. As the strength of the latter is accurately known, that of the ferrous sulphate is readily calculated.

To determine the concentration of chromic acid in the bath a sample equivalent to between 25 and 50 c.c. of 0.1 N_0 CrO_3 is employed. Thus if the bath is 2.5 M (250 g./l. of CrO_3) it is 7.5 N_0 *i.e.* 75 times as strong as 0.1 N_0 CrO_3 (or 0.1 N_0 $K_2Cr_2O_7$). Therefore a 0.5 c.c. sample may be taken, which is equivalent to

37.5 c.c. of 0.1 N_0 CrO_3. As it is not possible to measure accurately so small a volume as 0.5 c.c. this is obtained by diluting 10.0 c.c. of the bath sample to exactly 500 c.c., and taking 25.0 c.c. of this solution. This is diluted to 300 c.c., and 50.0 c.c. of $FeSO_4$ is added. The excess is then titrated with $KMnO_4$ as described above. From the $FeSO_4$ required to reduce the CrO_3, the strength of the latter can be computed.

Example.—Suppose 25.0 c.c. of $FeSO_4$ required 30.0 c.c. of $KMnO_4$. Then the $FeSO_4$ was 30.0/25.0 = 1.2 times as strong as the $KMnO_4$.

If now 50.0 c.c. of $FeSO_4$ was added to 25.0 c.c. of 0.1 N_0 $K_2Cr_2O_7$; and the excess of $FeSO_4$ required 28.8 c.c. of $KMnO_4$; the latter was equivalent to 28.8 /1.2 = 24.0 c.c. of $FeSO_4$. Therefore it required 50.0 − 24.0 = 26.0 c.c. of $FeSO_4$ to reduce 25.0 c.c. of 0.1 N_0 $K_2Cr_2O_7$. Therefore the $FeSO_4$ was 25.0/26.0 × 0.1 = 0.096 N_0.

If now to 0.5 c.c. (*i.e.* 1/2000 l.) of the plating bath 50 c.c. of $FeSO_4$ was added, and the excess $FeSO_4$ required 14.4 c.c. of $KMnO_4$, the latter was equivalent to 14.4/1.2 = 12.0 c.c. of $FeSO_4$. Hence the 0.5 c.c. bath sample required 50.0 − 12.0 = 38.0 c.c. of $FeSO_4$. Hence the bath was 38.0/0.5 = 76.0 times as strong as the $FeSO_4$. As the latter was 0.096 N_0, the original bath was 76.0 × 0.096 = 7.30 N_0. As, with respect to oxidation, the CrO_3 is trivalent (*i.e.*, it loses three valences when it is reduced) the solution is 7.3/3 = 2.43 M, and contains 243 g./l. or 32.4 oz./gal. of CrO_3.

(c) **Trivalent Chromium.**—In order to determine the content of trivalent chromium, the sample of plating bath is oxidized so that all the chromium is present as hexavalent chromium. This total chromium is then titrated as above. The difference between the total chromium and the hexavalent chromium originally present, represents the concentration of trivalent chromium. For the oxidation, the following reagents are required.

(*d*) Manganese sulphate solution, containing about 10 g./l. of $MnSO_4.4H_2O$.

(*e*) Silver nitrate solution, containing about 2.5 g./l. of $AgNO_3$.

(*f*) Ammonium persulphate solution, prepared by dissolving 10 g. of $(NH_4)_2S_2O_8$ in 100 c.c. of water. This solution is unstable and must be made just before use.

(*g*) Hydrochloric acid, 25 per cent by volume.

A 0.5 c.c. portion of the bath. *i.e.*, 25 c.c. of the 500 c.c. containing 10 c.c. of the bath sample, is diluted to 300 c.c., 25 c.c. of

concentrated H_2SO_4 added, and a few drops of the $MnSO_4$ solution. The solution is brought to boiling after adding several glass beads to prevent bumping. Ten cubic centimeters of the silver nitrate is added to catalyze the oxidation, and after that 20 c.c. of the persulphate solution. The appearance of a violet color due to permanganate indicates that the chromium is completely oxidized to chromic acid. If permanganate is not formed, more persulfate is added. The solution is then boiled for 10 min. and while still boiling, 5 c.c. of the dilute hydrochloric acid is added, and boiling is continued till the color of permanganate disappears. After cooling to room temperature, 50.0 c.c. of $FeSO_4$ is added, and the excess is titrated with permanganate as above.

Example.—Suppose that another 0.5 c.c. sample of the same chromium solution referred to on p. 312 was oxidized and titrated, and that the excess of ferrous sulphate required 12.0 c.c. of $KMnO_4$. This is equivalent to $12.0/1.2 = 10.0$ c.c. of $FeSO_4$. Therefore the total chromium required $50.0 - 10.0 = 40.0$ c.c. of $FeSO_4$. Hence the total chromium was $40.0/0.5 = 80.0$ times as strong as the $FeSO_4$. The latter was 0.096 N_0, hence the total chromium was equivalent to $80.0 \times 0.096 = 7.68\ N_0$. Therefore the trivalent chromium was equivalent to 7.68 − 7.30 (p. 312) = 0.38 N_0 CrO_3. But in neutralizing power, *e.g.* to form chromium sulphate, the trivalent chromium has the same equivalent as hexavalent chromium has with respect to oxidation. Therefore the trivalent chromium is also 0.38 N.

Of this trivalent chromium we may consider that sufficient is combined with the sulphate present to form chromium sulphate, $Cr_2(SO_4)_3$. If in this solution the sulphate was found to be 0.055 N, the chromium sulphate must also be 0.055 N. This corresponds to $0.055 \times \frac{392}{6} = 0.055 \times 65.3 = 3.6$ g./l. or 0.48 oz./gal. of $Cr_2(SO_4)_3$.

The balance of the trivalent chromium, *i.e.*, $0.38 - 0.055 = 0.32\ N$ is presumably present as a chromium chromate. Until however a definite formula for this compound is established it is not advisable to calculate its actual concentration. For purposes of comparison the normality may be used, or the equivalent in g./l. of the metal chromium, Cr, or of chromic oxide, Cr_2O_3. As the equivalent weight of trivalent chromium is $52/3 = 17.3$, the above value corresponds to $0.32 \times 17.3 = 5.62$ g./l. or 0.75 oz./gal. of trivalent chromium in addition to that present as sulphate. The molecular weight of Cr_2O_3 is 152 and its equivalent weight is $152/6 = 25.3$. Therefore the above amount of trivalent chromium corresponds to $0.32 \times 25.3 = 8.1$ g./l. or 1.1 oz./gal. of Cr_2O_3.

If we assume that a definite chromium chromate such as $Cr(HCrO_4)_3$ is formed, it is possible to calculate the amount of the chromic acid that is thereby "combined." In the above illustration, this would correspond with 0.32 M CrO_3, as (according to the above formula) the chromic acid is acting in this compound as a mono-basic acid. The "free" chromic acid would then be 2.43 (p. 312) − 0.32 = 2.11 M, *i.e.*, 211 g./l. or 28.1 oz./gal.

It is also possible to determine the trivalent chromium directly by the following method.

(d) **Iron and Trivalent Chromium.**—Dilute 25 c.c. of the plating solution to about 200 c.c., and add a slight excess of ammonium hydroxide. This precipitates all the iron as ferric hydroxide (or possibly a basic ferric chromate), together with the trivalent chromium, which may also be precipitated as hydroxide or basic chromate. The solution is heated to boiling, allowed to settle and filtered. The precipitate is washed with hot water, dissolved in dilute sulphuric acid and again precipitated with ammonia. This second precipitation removes practically all of the hexavalent chromium carried down in the first treatment. The precipitate is again dissolved in dilute sulphuric acid, and an excess of sodium hydroxide is added, followed by a few cubic centimeters of hydrogen peroxide or of bromine water. This oxidizes the trivalent chromium to soluble sodium chromate. The solution is boiled and filtered, and the precipitate of ferric hydroxide is washed with hot water. It is again dissolved in dilute sulphuric acid and treated with sodium hydroxide and hydrogen peroxide or bromine, filtered, thoroughly washed, ignited and weighed as ferric oxide, Fe_2O_3, which contains 70 per cent of iron. The filtrates from the last two iron precipitates are combined and acidified with sulphuric acid, of which 25 c.c. excess is added. The solution is boiled to destroy the peroxide, and cooled. It is then titrated for hexavalent chromium just as on p. 311, and the result is calculated to its equivalent of trivalent chromium.

Example.—Iron.

Suppose that 25 c.c. of the chromium bath yielded 0.0832 g. of Fe_2O_3. This is equivalent to $0.0832 \times 0.70 = 0.0582$ g. Fe

$0.0582 \times \frac{1000}{25} = 0.0582 \times 40 = 2.33$ g./l. Fe or $2.33 \times 0.134 =$ 0.30 oz./gal. Fe.

Trivalent Chromium.—Suppose that to the solution containing the chromate obtained from the trivalent chromium in a 25 c.c. sample of plating solution, was added 50 c.c. of the ferrous ammonium sulphate solution (p. 312) and the excess required 6.0 c.c. of the $KMnO_4$. The latter is equivalent to $6.0/1.2 = 5.0$ c.c. of the ferrous sulphate. Therefore the chromate required $50.0 - 5.0 = 45.0$ c.c. of $FeSO_4$. As the latter was 0.096 N_0, the chromate, (derived from the trivalent chromium in 25 c.c. of the bath), must be $\frac{45}{25} \times 0.096 = 0.173$ N_0. Therefore the Cr^{III} content is also 0.173 N_0, which corresponds to $0.173 \times \frac{52}{3} = 2.99$ g./l. or 0.4 oz./gal. of trivalent chromium.

(e) **Stripping Chromium Deposits.**—It may be necessary to dissolve off chromium deposits either for the purpose of replating, or of determining the weight and hence the average thickness of the coating.

(1) *For Replating.*—Chromium may be dissolved from brass or nickel by treatment with warm dilute hydrochloric acid, *e.g.*, one part by volume of concentrated hydrochloric acid to ten of water. Chromium may also be removed from brass by using a reverse current in 90 per cent sulphuric acid at room temperature. This treatment also removes nickel (p. 274) so it may be used for stripping brass that has been plated with both nickel and chromium.

Treatment with hydrochloric acid can also be used on steel, but care must be exercised to remove the articles as soon as the chromium is dissolved, as the hydrochloric acid may attack the steel. To remove chromium from steel, it is preferable to make the articles anodic in a chromic acid solution, (*e.g.*, in a chromium bath); or still better in a sodium hydroxide solution, containing *e.*g., 45 to 60 g./l. (6 to 8 oz./gal.) of NaOH. The latter method is the safest way of stripping steel to avoid any etching of the base metal. To avoid pitting of the steel, the articles should be moved during the stripping.

(2) *For Determining the Chromium.*—Chromium may be dissolved from brass or nickel plated brass by treatment with warm dilute hydrochloric acid, *e.g.*, 1 part to 19 of water, at about 50°C. (122°F.); without any measurable attack of the base metal. The weight of chromium is then equal to the loss in weight. The anodic alkali treatment is quantitative for steel. If chromium is dissolved with hydrochloric acid from iron or steel, aluminum or zinc, or their alloys, it is necessary to determine the chromium in the solution, as the acid may attack these base metals, even though they are nickel plated.

To determine the chromium, the solution is evaporated to a small volume to expel most of the hydrochloric acid. It is then diluted, neutralized with sodium hydroxide, and bromine or hydrogen peroxide is added to oxidize the chromium. The solution is boiled, acidified with sulphuric acid and again boiled. The chromic acid formed is then titrated with ferrous sulphate as above.

CHAPTER XVII

DEPOSITION OF ZINC AND CADMIUM

Zinc and cadmium resemble each other both chemically and electrochemically, and hence the solutions and conditions used for their deposition are very similar. The two metals are associated together in nature; in fact, most of the commercial supplies of cadmium are recovered as by-products in zinc refining. Zinc is by far the more common and the cheaper of the two and only within very recent years has the deposition of cadmium been even attempted upon a commercial scale. The relative advantages of these two metals were considered (page 122) in connection with the selection of electroplating.

1. ZINC DEPOSITION

The deposition of zinc is an interesting subject for investigation and should be studied much more exhaustively than it has been, not alone because of its technical importance in zinc refining and in plating, but also because, through its study, light may be thrown upon the deposition of other metals. Zinc forms many soluble salts and it can be deposited, under some conditions at least, from its sulphate, chloride, and acetate solutions, and from the alkaline zincates and double cyanides. Therefore, practically every type of bath used for any other metal may be applied to zinc, thus permitting many interesting comparisons. The deposits are especially susceptible to the effect of foreign substances, both inorganic and organic, and hence through studies of these effects light may be thrown upon the general functions of addition agents.

The two principal types of bath used for zinc plating are the acid sulphate solutions and the alkaline cyanide solutions. Satisfactory deposits can be produced from either type, but the cyanide solutions possess better "throwing power" and are hence most useful for parts with deep recesses.[1] The deposits from the sulphate solution produced under favorable conditions in the

[1] Horsch, W. G., and Fuwa, T., *Trans. Am. Electrochem. Soc.*, vol. 41, p. 363, 1922.

presence of addition agents are usually brighter than those obtained from the alkaline solutions. As, however, the principal function of zinc coatings is for protection and not for appearance, no great weight should be attached to the latter. In the case of zinc coatings more than those of most metals, purity is an important consideration, as even small amounts of foreign metals, such as nickel, lead, tin, and copper, may appreciably accelerate the atmospheric attack of the zinc and hence reduce its protective value. In this respect the sulphate solutions are more satisfactory than the cyanide, as there is less tendency for metallic impurities from the anodes to pass into the deposits in a sulphate than in a cyanide solution, in which latter the potentials of many of these metals are very close. An example of this behavior is seen in brass plating, in which the metals zinc and copper are simultaneously deposited from their cyanide solutions, an operation which would be practically impossible in acid solutions. It is therefore even more important to use pure zinc anodes in the cyanide than in the sulphate solutions.

One drawback to the use of the usual cyanide zinc solutions is that they do not plate satisfactorily upon cast iron. When this is attempted, a very low cathode efficiency is secured, and poor, streaked deposits are obtained. It is probable that this behavior is due to the presence of the carbon or graphite in the iron, and to the low overvoltage of hydrogen on carbon. Somewhat better deposits are obtained in heated solutions at very high current densities, but at best the results are far from satisfactory. In a recently used method a small amount (not over 2 per cent of the zinc content) of mercuric oxide or cyanide is dissolved in the cyanide zinc bath, and zinc anodes containing about 1 per cent of mercury are used. Deposition on cast iron is readily conducted and bright deposits are obtained. The effect of the mercury, of which a small amount passes into the deposit, is probably due to a change in the hydrogen overvoltage.

It is also possible to plate on cast iron by using a zinc cyanide solution containing a small amount of cadmium; or by first striking in a cadmium solution and then plating in the zinc bath.

A. Sulphate Solutions

It is possible to obtain fairly satisfactory deposits of zinc from slightly acidified zinc sulphate solutions with no other additions, and such solutions are not infrequently employed. Owing

to the fact that zinc dissolves readily as anode in such solutions, there is no difficulty in maintaining the metal content. Instead of tending to become more acid, as does a pure nickel sulphate solution with nickel anodes, a zinc solution tends to become less acid and hence fresh additions of acid are required at intervals. This is because the zinc dissolves not only electrochemically, *i.e.*, as anode, but also chemically, *i.e.*, by direct replacement of hydrogen in the dilute sulphuric acid present. This can be readily observed by noting the evolution of hydrogen from the zinc anodes when no current is passing. This behavior is taken advantage of in maintaining the metal content of the solution. Instead of adding zinc sulphate at intervals to replace that lost mechanically, sulphuric acid is added, and by the gradual chemical solution of the zinc, additional zinc sulphate is formed in the solution. The term "self-sustaining" sometimes applied to such solutions indicates simply that the required zinc salt is made in the bath instead of being added to it. In some cases a new bath is even prepared by the solution of zinc in the requisite amount of sulphuric acid. Whether such a procedure is warranted will depend upon the relative costs of sulphuric acid, zinc, and zinc sulphate.

1. Function of Constituents

Although fairly satisfactory zinc deposits can be secured from solutions containing only zinc sulphate and sulphuric acid, the desire to improve the quality of the deposit and the rate of deposition have led to the addition of a large variety of substances. In various texts[1] numerous formulas for acid zinc plating solutions are given, besides a list of specific addition agents. Examination of these and other published formulas shows that most of the substances used serve one or more of the purposes referred to in previous chapters. They will therefore be considered in connection with their probable functions.

(a) **To Furnish the Metal Concentration.**—The most commonly used salt for these baths is zinc sulphate ($ZnSO_4.7H_2O$), although the chloride ($ZnCl_2$) has been occasionally employed. Both of these materials are very cheap and the usual choice of zinc sulphate rests upon the fact that it is a crystallized salt, and that it can therefore be secured in a relatively purer state than

[1] Flanders, W. T., "Galvanizing and Tinning," David Williams Co., New York, 1916.

the zinc chloride. The commercial zinc sulphate consists of white crystals, which are not likely to contain any large amount of foreign metals. Lead can not be present in appreciable amount because lead sulphate is insoluble. Copper is not likely to be present, as any copper will be precipitated out during the solution of zinc in sulphuric acid. Iron may be present in at least small amounts, but is probably not harmful, at least it is known that good zinc deposits can be obtained from solutions containing appreciable amounts of iron. Therefore no very rigid specifications are necessary for securing this salt of the requisite purity.

Zinc sulphate is very soluble in water, so that it is possible to use concentrated solutions. It is not unusual to employ solutions containing as much as 360 g./l. (48 oz./gal.) of the crystallized salt, *i.e.*, 2.5 *N*, and even stronger solutions have been employed. In most cases the solutions contain from 150 to 300 g./l. (20 to 40 oz./gal.) *i.e.*, they are from about 1 to 2 *N*.

Zinc chloride is most commonly sold as the anhydrous salt, which contains when pure, 48 per cent of zinc, as compared with 23 per cent in the crystallized zinc sulphate. As the price of the chloride is about twice that of the sulphate, the cost is about equal for preparing solutions with a given zinc content. As however the chloride is more difficult to obtain pure, the sulphate is commonly used, even when a high chloride content is desired, which is then obtained by adding sodium or ammonium chloride.

(b) **To Increase Anode Corrosion.**—Since, as above mentioned, zinc anodes corrode readily in these solutions, especially if they contain the usual amount of free acid, no additions are necessary for the specific purpose of increasing anode corrosion.

(c) **To Increase the Conductivity.**—Most of the inorganic substances added to zinc sulphate solutions increase the conductivity to some extent, which is desirable, because, as previously noted, all the bivalent metal sulphates (such as those of zinc, nickel, copper, magnesium, etc.) have relatively high resistivities. In a recent study of acid zinc solutions[1] it was found that by adding sodium or ammonium chloride to either zinc sulphate or chloride solutions, the conductivity can be greatly increased. Concentrations up to 4 *N* ammonium chloride, *i.e.*, 214 g./l. or 29 oz./gal. of NH_4Cl, were suggested. In unpublished experiments, the same author has obtained good

[1] THOMPSON, M. R., *Trans. Am. Electrochem. Soc*, vol. 50, p. 193. 1926.

results with zinc sulphate solutions containing sodium sulphate in fairly high concentrations. One objection to high chloride solutions is that they corrode the contacts; and another is that the articles must be very thoroughly rinsed to avoid subsequent corrosion of the zinc coating. Additions of sodium or ammonium sulphate or chloride increase the conductivity and reduce the treeing or roughness.

Other salts, such as magnesium sulphate ($MgSO_4.7H_2O$) or aluminum sulphate ($Al_2(SO_4)_3.18H_2O$), which are frequently added, have no more effect upon the conductivity than would be produced by an equivalent amount of zinc sulphate.

(d) **To Decrease the Metal Ion Concentration.**—The addition of any soluble sulphate, such as sodium, magnesium, or aluminum sulphate to a zinc sulphate bath, reduces the metal ion concentration to a certain extent. In nickel solutions such additions cause a marked increase in cathode polarization and consequently in throwing power. With zinc sulphate however the increase in polarization is so small as to have no appreciable effect on the throwing power. Thompson in the study referred to above, was unable to produce any significant increase in the throwing power of acid zinc baths.

(e) **To Regulate the Acidity.**—It is well known that zinc solutions must be slightly acid in order to produce dense deposits free from oxides or basic salts and also that they must not be too acid, otherwise the cathode efficiency is low, and pitted or spongy deposits are produced. As noted on page 74, it is possible to deposit zinc from acid solutions only because of the appreciable overvoltage of hydrogen on zinc. The maintenance of the proper acidity in zinc solutions is more difficult than in nickel solutions, in spite of the fact that a wider range of acidity is permissible. The difficulty arises from the above-mentioned fact that part of the zinc from the anodes dissolves chemically and thus reduces the acidity of the solutions during operation or on standing when not in use. In consequence, it is necessary to make frequent additions of acid to the baths to maintain a definite acidity.

The experience[1] with zinc winning baths with insoluble anodes, indicates that if the solutions are free from foreign metals, especially cobalt and nickel, it is possible to secure good deposits and

[1] Ralston, O. C., "Electrolytic Deposition and Hydrometallurgy of Zinc." McGraw Hill Book Company, Inc., 1921.

high cathode efficiencies at high current densities in strongly acid solutions, containing even as much as 50 to 100 g./l. (6.7 to 13.4 oz./gal.) of sulphuric acid. These conditions have not been found practicable in zinc plating, however, and best results are usually obtained with a pH of 3.5 to 4.5. For measuring the pH of such solutions, brom phenol blue is satisfactory. As noted on p. 270, colorimetric pH readings are usually higher than electrometric readings in fairly concentrated salt solutions. As no actual values of the salt correction for brom phenol blue in zinc solutions have been published it will be necessary to make such measurements before the true pH can be stated. The values given are colorimetric, uncorrected.

If sulphuric acid is added in appreciable amount to a zinc solution it produces a high acidity (low pH) and hence increases the rate of secondary anode corrosion. In consequence, the acid is rapidly neutralized, and within the working day there may be a great change in acidity and, consequently, variation in the quality of the work. If, on the other hand, a weak acid is added, even in considerable amount, it will produce a smaller increase in acidity; hence secondary anode corrosion will be slower, and there will be less change in acidity in a given period.

Two acids that have been added for thus regulating the acidity are acetic acid ($HC_2H_3O_2$), and boric acid (H_3BO_3). Of these, acetic acid is preferable, because, although weaker than sulphuric, it is decidedly stronger than boric acid. Boric acid is so weak that it is unlikely that it serves any useful purpose in a zinc solution, *i.e.*, it cannot produce any buffer action in a solution with a pH as low as 3.5. Instead of adding acetic acid, directly to the solution, it is customary to add sodium acetate, usually purchased as the crystallized salt ($NaC_2H_3O_2.3H_2O$). Whenever sulphuric acid is then added, it liberates an equivalent amount of acetic acid, thus producing a higher pH (lower acidity) than if no acetate were present. As the function of the sodium acetate is primarily to serve as a "buffer" and thus to regulate the acidity of the solutions, it may be added in considerable amounts without producing marked effects upon their operation. Concentrations of from 15 to 30 g./l. (2 to 4 oz./gal.) are often employed, *i.e.*, from about 0.1 to 0.2 *N*.

The experiments of Thompson indicate that the principal beneficial effect of aluminum sulphate or chloride in a zinc solution is due to its buffer action. In the concentrations of

aluminum salts commonly used, aluminum hydroxide begins to precipitate at a pH of about 4. In such solutions the appearance of a white gelatinous precipitate is evidence that the pH is at least 4. So long as any appreciable amount of aluminum salt remains in solution, the pH cannot exceed 4.5, as any decrease in acidity, *e.g.* through chemical solution of the zinc anodes, simply causes more aluminum hydroxide to precipitate. This in turn can be re-dissolved by the careful addition of hydrochloric or sulphuric acid. An additional advantage of the aluminum salt is that it retards the action of the free acid upon the zinc anodes when no current is passing.

(f) **As Addition Agents.**—A very large number of substances have been employed in zinc solutions for the purpose of improving the structure or luster of the deposits. Among the most commonly used are reducing substances, such as dextrose (glucose), glycerin, tannic acid, and tartaric acid; and colloids, such as gelatin, dextrin, and gum tragacanth. Many of the substances employed may contain several constituents. Thus when corn syrup or glucose syrup is used, it contains not only the reducing sugars but also appreciable amounts of dextrin. Licorice, which is often employed, contains "glucosides" (compounds which yield glucose on decomposition) and also certain resins which probably serve as colloids. Naphthalene compounds have also been used.

In addition to regulating the acidity, an aluminum salt may serve as an inorganic addition agent through the formation of colloidal aluminum hydroxide, especially near the cathode. Careful tests have shown that zinc deposits obtained from solutions containing aluminum have none of this metal in them. Its effects in producing finer and brighter deposits of zinc are probably due to the control of pH and to a slight increase in cathode polarization. From 15 to 30 g./l. (2 to 4 oz./gal.) of the crystallized salt, $Al_2(SO_4)_3.18H_2O$, (or an equivalent amount of $AlCl_3$) is often employed, which makes the solutions approximately 0.15 to 0.3 *N*. It is interesting to note that in the early years when solutions containing zinc sulphate and a large amount of aluminum sulphate were used for plating it was claimed by some that the deposited metal was aluminum. It is doubtful whether aluminum can be deposited from aqueous solutions under any conditions.

2. Zinc Anodes

Zinc anodes are cast or extruded. Various grades of purity are available commercially, with corresponding differences in price. It is desirable to use zinc anodes of high purity, *i.e.*, practically free from lead, copper, tin, antimony, arsenic, etc. Such metal can be produced from the ores in the eastern United States, or by electrolytic refining of the zinc from western ores. Even if the impurities do not readily pass into the deposit when the acid solutions are used, their presence is objectionable because they tend to accelerate (by forming local "couples") irregular corrosion and waste of the anodes. There is no great difficulty in securing zinc anodes containing 99 per cent of zinc. The use of anodes made from scrap zinc, and often containing large amounts of impurities, does not appear warranted, especially when it is realized that the actual cost of the zinc represents so small a proportion of the cost of the plating operation. The use of pure zinc anodes is even more desirable in the cyanide and chloride than in the sulphate solutions.

3. Operating Conditions

(a) **Temperature.**—There seems to be no marked advantage in heating the acid zinc plating solutions, and they are therefore usually operated at ordinary temperature. The effect of an elevation in temperature is to produce coarser deposits, just as with other metals. With moving cathodes, at high current densities, fine-grained deposits can be produced in warm solutions containing suitable addition agents.

(b) **Current Density.**—Zinc plating in cold, still sulphate solutions is usually conducted with a current density of 1.5 to 3 amp./dm.^{2} (14 to 28 amp./sq. ft.). In warm, agitated solutions with addition agents current densities up to 10 amp./dm.^{2} (93 amp./sq. ft.) are used. Especially when the solutions are fairly acid, it is found that brighter and more continuous deposits are produced at the higher current density. In such solutions the current efficiency increases with increased current density, up to the point at which the metal concentration is not maintained at the cathode. This is because, apart from the high overvoltage of hydrogen on zinc, it is easier to deposit hydrogen than zinc from solutions containing both ions. Hence at very low current densities a larger proportion of hydrogen is discharged than at higher current densities.

In zinc solutions with additional chloride or sulphate and hence with a high conductivity, current densities up to 5 amp./dm.^{2} (47 amp./sq. ft.) may be employed in still solutions, and up to 10 amp./dm.^{2} (93 amp./sq. ft.) in well agitated baths, without producing roughness.

Zinc deposits often show pitting, but are not subject to brittleness or cracking, such as occurs with nickel. It is probable that the pitting is due to many of the same causes as in nickel plating (page 243). Although it is most often produced when the solutions are too acid, there are other important factors. Among these, in the case of zinc, is the presence of even small amounts of foreign metals in the solution. In zinc refining solutions it is known that even minute traces of nickel or cobalt may cause very great losses in cathode efficiency, probably because the hydrogen overvoltage is much lower upon them than upon zinc.

4. Suggested Formulas

The following are typical formulas for acid zinc baths. As previously noted, a large number of substances may be added, and almost innumerable formulas have been proposed. About the same effects are obtained with sodium chloride and ammonium chloride. In these and most other plating formulas, the exact concentrations are not important.

	N	g./l.	oz./gal.
1. Zinc sulphate ($ZnSO_4.7H_2O$)....	1.7	240	32
Ammonium chloride (NH_4Cl)	0.3	15	2
Aluminum sulphate, $Al_2(SO_4)_3.18H_2O$.....	0.25	30	4
Licorice.....	....	1	0.13
2. Zinc chloride ($ZnCl_2$).....	2.0	136	18
Sodium chloride (NaCl).....	4.0	234	32
or ammonium chloride (NH_4Cl)	4.0	214	28
Aluminum chloride ($AlCl_3.6H_2O$)	0.25	20	3
3. Zinc sulphate ($ZnSO_4.7H_2O$)....	3.0	410	54
Sodium sulphate (Na_2SO_4).....	1.0	75	10
Aluminum chloride ($AlCl_3.6H_2O$)	0.25	20	3
4. Zinc sulphate ($ZnSO_4.7H_2O$)....	2.50	360	48
Ammonium chloride (NH_4Cl)...	0.60	30	4
Sodium acetate ($NaC_2H_3O_2.3H_2O$).....	0.10	15	2
Glucose.....	....	120	16

In all of these solutions a small amount of concentrated sulphuric acid (or hydrochloric acid in No. 2.) is added at intervals, usually once a day. The amount to be added may be determined approximately by titration or by pH measurements.

5. Analysis of Solutions

There is no difficulty in determining in such solutions, when desired, zinc, ammonia, chloride, magnesium, aluminum and iron, and pH. There is no simple chemical method for the determination of acetic acid (or acetate).

(a) **Zinc.**—This is most conveniently estimated by the volumetric ferrocyanide method, in which a standard solution of potassium ferrocyanide, $K_4Fe(CN)_6$, is run into the acidified solution, producing a precipitate which is a mixture of potassium zinc ferrocyanide, $K_2ZnFe(CN)_6$ and zinc ferrocyanide, $Zn_2Fe(CN)_6$. The end point is detected by testing a drop of the solution with uranium acetate, used as an outside indicator.

The ferrocyanide solution may be conveniently made so that 1 c.c. is equal to approximately 0.005 g. of zinc. This may be prepared by dissolving 22 g. of the crystallized salt, $K_4Fe(CN)_6.3H_2O$ in water and diluting to 1 l. It can be standardized most conveniently against C. P. zinc, such as can be purchased in a granular condition (20 mesh). Zinc dust is not sufficiently pure for this purpose. About 0.2 to 0.25 g. of the metal is weighed accurately, and is dissolved carefully in dilute hydrochloric acid. The solution is diluted to 100 c.c., and about 5 c.c. of concentrated hydrochloric acid and 5 g. of ammonium chloride are added. The solution is then heated to about 80°C. (176°F.), and the ferrocyanide solution is run in gradually while the solution is stirred vigorously. As the approximate strength of the ferrocyanide solution and the weight of the zinc are known, the volume that will be required can be roughly estimated. If it is thought that about 40 c.c. may be required, run in 35 c.c., and then test a drop of the solution by placing it on a porcelain "spot plate" with a drop of the uranium acetate solution. (This is prepared by dissolving about 1 g. of the uranium acetate crystals in 10 c.c. of water.) If a brown color is produced, an excess of ferrocyanide has been added and the titration must be repeated, using a smaller volume of ferrocyanide before making the initial test. If no brown color is produced, run in about 0.2 c.c. more of the ferrocyanide, and, after stirring,

again test the solution. Continue these additions until a faint brown color is produced within 1 min. This represents the end point of the titration.

The determination of zinc in the plating solution is carried out by the same procedure. Fortunately, there are not likely to be in these solutions any appreciable amounts of interfering elements. Therefore a 5-c.c. sample can be diluted to 100 c.c., and 5 c.c. of concentrated hydrochloric acid and 5 g. of ammonium chloride added, the solution heated, and the titration carried out as above till the end point is secured. If much iron is present, it should be removed by precipitation with ammonia. Aluminum does not interfere.

Example.—Suppose that in standardizing, two determinations were made in which the weights of zinc were respectively 0.212 and 0.236 g., and that the volumes of ferrocyanide used in the titrations were 42.2 and 47.6 c.c. respectively. Then 1 c.c. of the solution is equal to:

$$\frac{0.212}{42.2} = 0.00502 \text{ g.}$$

or

$$\frac{0.236}{47.6} = 0.00496 \text{ g.}$$

$$\text{Average} = 0.00499 \text{ g.}$$

If then a 5-c.c. sample (1/200 l.) of the plating solution required for its titration 47.3 c.c. of the ferrocyanide, it must contain $47.3 \times 0.00499 \times 200 =$ 47.2 g./l. (6.3 oz./gal.) of zinc. This is equivalent to $\frac{287.6}{65.4} \times 47.2 = 208$ g./l. (27.9 oz./gal.) of zinc sulphate ($ZnSO_4.7H_2O$).

(b) **Ammonia.**—This may be determined by distillation with alkali into an excess of standard acid. The method and calculation are exactly similar to that described for nickel (page 263).

(c) **Iron and Alumina.**—The sample of solution, *e.g.*, 25 c.c., is diluted to 100 c.c., a few drops of nitric acid are added, the solution boiled, and the iron and aluminum precipitated as hydroxides with a slight excess of ammonia. The precipitate is washed with hot water, dried, ignited, and weighed as $Fe_2O_3 + Al_2O_3$. If iron is present in appreciable amount the ignited oxides will be distinctly yellow or brown. If so, the iron may be determined in a separate portion of the solution by reducing with zinc and titrating with standard permanganate, $KMnO_4$. The iron thus found is calculated as Fe_2O_3, and this weight is deducted from the combined weight of Fe_2O_3 and Al_2O_3. The latter is then calculated to $Al_2(SO_4)_3.18H_2O$,

to alum, $K_2SO_4.Al_2(SO_4)_3.24H_2O$, or to $AlCl_3.6H_2O$; according to which compound has been added.

(d) **Magnesium.**—In order to determine magnesium it is necessary first to precipitate the zinc from the solution, which may be done either with ammonium sulphide or with hydrogen sulphide in a solution slightly acidified with acetic acid. After the precipitated zinc sulphide is filtered out, the solution is boiled and the magnesium is precipitated in the usual way by the addition of ammonium chloride, ammonium phosphate, and ammonia. The precipitate, which consists of magnesium ammonium phosphate ($MgNH_4PO_4$), is filtered out, washed with dilute ammonia, ignited, and weighed as magnesium pyrophosphate ($Mg_2P_2O_7$). The content of magnesium sulphate ($MgSO_4.7H_2O$) is then calculated by multiplying the weight of $Mg_2P_2O_7$ by the factor 1.11, derived from the ratio $Mg_2P_2O_7 : MgSO_4.7H_2O$.

(e) **Chloride.**—This may be determined either by volumetric titration with silver nitrate (page 47) or by the gravimetric precipitation (page 37). If a high concentration is present, *e.g.* 4 *N* NaCl, its concentration can be computed approximately from the specific gravity and zinc content.

(f) **Acidity.**—In the absence of weak acids, such as acetic or boric acid, the free sulphuric or hydrochloric acid can be approximately titrated with methyl orange as the indicator. With weak acids present it is better to measure the pH by colorimetric comparisons with indicators, such as brom phenol blue.

B. Alkaline Zinc Solutions

1. Functions of Constituents

It is interesting to note that although zinc may exist in solution either as zincate, *e.g.*, $Zn(ONa)_2$ or Na_2ZnO_2 (or, more strictly speaking, $NaHZnO_2$), and as the double cyanide, $Zn(CN)_2.2NaCN$ or $Na_2Zn(CN)_4$, neither of these solutions is so satisfactory for plating as is a mixture of the two. If zinc cyanide, $Zn(CN)_2$, is dissolved in sodium cyanide, the double cyanide is formed:

$$Zn(CN)_2 + 2NaCN = Na_2Zn(CN)_4$$

If, in place of the sodium cyanide, sodium hydroxide is used, part of the zinc is converted to zincate:

$$2Zn(CN)_2 + 4NaOH = Na_2Zn(CN)_4 + Na_2ZnO_2 + 2H_2O$$

If it is desired to have a considerable amount of alkaline hydroxide or zincate present in the solution, the same result can be accomplished by dissolving zinc oxide (ZnO) in sodium cyanide

$$2ZnO + 4NaCN = Na_2Zn(CN)_4 + Na_2ZnO_2$$

Whether the use of zinc oxide and sodium cyanide represents an economy over that of corresponding amounts of zinc cyanide and sodium hydroxide will depend upon the relative costs of the four materials. Assuming that the same composition of solution is actually secured, it is immaterial from the standpoint of operation as to what materials are used in its preparation.

We may consider that in any such solutions the principal constituents are (*a*) sodium zinc cyanide, $Na_2Zn(CN)_4$, (*b*) sodium zincate (Na_2ZnO_2), (*c*) excess sodium cyanide, (*d*) excess sodium hydroxide, and (*e*) sodium carbonate. Whether the last compound is intentionally added or not, it is certain to be present in solutions that have been operated for any period, as it is formed by decomposition of cyanide and by absorption of carbon dioxide from the air by the free alkali in the solution.

It is difficult to state the exact effect or best concentration of each of the above constituents. Two investigations conducted in recent years[1] yielded results that are in part contradictory, largely for the reason that the studies were not conducted with similar solutions, and neither covered the entire field. A more exhaustive investigation is required before final conclusions can be drawn.

In general, it appears that the desirable concentration of zinc is between 30 and 45 g./l. (4 and 6 oz./gal.), *i.e.*, the solutions are from 1 to 1.5 *N*. A considerable portion of this may be present as zincate and the remainder as double cyanide. It is desirable to have present in the solution an excess of cyanide or hydroxide. In any solution containing both zincate and double cyanide it is impossible to state whether any excess alkali present is cyanide or hydroxide. Speculation as to whether it is better to have in such mixed solutions an excess of cyanide or of alkali is therefore idle. Thus, if a solution were *N* in zinc, it would require that the total cyanide should be equivalent to 2 *N* to form $Na_2Zn(CN)_4$, or the total alkali equivalent to

[1] Blum, W., Liscomb, F. J., and Carson, C. M., Zinc cyanide plating solutions, Bureau of Standards, *Tech. Paper 195*, 1921; and Wernlund, C. J., *Trans. Am. Electrochem. Soc.*, vol. 40, p. 345, 1921.

2 N to form Na_2ZnO_2. If in a given solution, N in zinc, the total cyanide were 1.5 N, and the total alkali (ZnO + NaOH) were 1.5 N, the solution could with equal correctness be considered as (*a*) 0.5 N in both double cyanide and in zincate, with an excess of 0.5 N both of free cyanide and alkali; or (*b*) as 0.75 N in double cyanide, 0.25 N in zincate, and 1 N in free alkali; or (*c*) as 0.25 N in double cyanide, 0.75 N in zincate, and 1 N in free cyanide. It is therefore difficult and sometimes confusing to compare the results obtained with solutions which have been prepared or analyzed by different methods. For simplicity, we may assume that the zinc first forms the double cyanide, and forms zincate only if the cyanide is insufficient. By this arbitrary method of expression a solution cannot contain both zincate and "free cyanide."

An appreciable excess of cyanide or of alkali is desirable in the solution. They both tend to produce finer deposits, probably through a reduction of the zinc ion concentration below the necessarily small value present in solutions containing complex cyanides. Moreover, they tend to aid anode corrosion, and especially to keep in solution the products such as zinc cyanide or hydroxide formed at the anode. A large excess of cyanide or alkali is, however, to be avoided, as it reduces the cathode efficiency and is likely to cause porous or spongy deposits.

There is some doubt as to the effect of carbonate in the solution. In the limited experiments conducted at the Bureau of Standards, the presence of sodium carbonate in amounts as small as 15 g./l.(2 oz./gal.), *i.e.*, about 0.25 N, was found slightly detrimental, and large amounts produced decidedly porous deposits. Wernlund, on the other hand, found that solutions with an appreciable content of carbonate operate more satisfactorily, especially with respect to uniform anode corrosion. Even if small amounts are harmless, it seems certain that much larger concentrations of carbonate, such as are produced by long operation, especially of heated solutions, are detrimental. The content may be decreased by cooling the solutions to a temperature of −5°C. (23°F.) or lower (page 227).

Various additions have been proposed for use in zinc cyanide solutions and it is difficult to account for the function of each, or to state how effective each may be. Certain of them have been used primarily for improving the appearance or luster of the deposits, which is desirable but does not necessarily add to

their protective value. Recent evidence indicates that certain of these addition agents may increase the throwing power. As previously noted (page 317), mercury compounds are sometimes added to the solution. Alum or aluminum sulphate has been sometimes used. In alkaline solutions it forms aluminates, such as $NaAlO_2$, and may also be present in part as a colloidal solution of aluminum hydroxide. Whether in such a solution the hydroxide migrates to, or is absorbed by, the cathode, is not known. The same uncertainty exists regarding certain gums that have been employed. Fluorides have also been recently suggested for use in such baths. Even if such additions prove beneficial, it appears desirable to restrict their use to that one which in a given case is most beneficial. At best it is very difficult to analyze a zinc cyanide solution and it is absolutely impossible to determine by present methods certain organic additions. If, therefore, two or more are present, it is not even possible to tell from the appearance of the deposits which is lacking or which may be in excess. In any case there is not so great a need for addition agents in the cyanide solutions as in the sulphate, as without addition agents the deposits from cyanide solutions are finer grained than although not so bright as those from sulphate solutions without such agents.

2. Operating Conditions

(a) **Temperature.**—These solutions are found to give better results at slightly elevated temperatures, *e.g.*, 40 to 50°C. (104 to 122°F.), even though the actual size of the crystals may be larger than in cold solutions. Very high temperatures are objectionable, as they cause excessive decomposition of cyanide. The warm solutions are advantageous because of the increased conductivity.

(b) **Current Density.**—It is not customary to employ as high current densities in cyanide as in sulphate solutions. Best results with simple solutions are obtained at from 1 to 2 amp./dm.^{2} (9.3 to 19 amp./sq. ft.). With solutions containing addition agents it is, however, possible to use higher current densities, up to 6 amp./dm.^{2} (56 amp./sq. ft.).

3. Suggested Formulas

The work of the Bureau of Standards indicated the following as a convenient satisfactory formula. It is not essentially dif-

ferent from many formulas previously used in commercial plating, and represents a "high alkali" solution. The same composition is secured whatever method of preparation is employed.

In this as in other similar cases, the concentrations given have been rounded off to be equivalent to a simple number of ounces per gallon and allowances have been made for the amounts of impurities likely to be present in commercial chemicals.

(1)	Approx. N	g./l.	oz./gal.
Zinc cyanide, $Zn(CN)_2$	1.0	60	8
Sodium cyanide (NaCN)	0.5	23	3
Sodium hydroxide (NaOH)	1.3	53	7
or			
Zinc oxide (ZnO)	1.0	45	6
Sodium cyanide (NaCN)	1.5	75	10
Sodium hydroxide (NaOH)	0.3	15	2

Such a solution may be considered as being 1.5 N in total cyanide, and 1.3 N in total alkali, and therefore as containing 0.75 N $Na_2Zn(CN)_4$, 0.25 N Na_2ZnO_2, and 0.8 N free NaOH.

The following formula[1] representing a "low alkali" solution was suggested by Wernlund. As previously noted, this formula appears to be somewhat complicated. As it was found to give white smooth deposits, free from stains, it is included here, with the tentative proposal that those using it should try, if possible, to reduce the number of addition agents employed.

(2)	N	g./l.	oz./gal.
Zinc cyanide	1.00	60.0	8
Sodium cyanide	1.00	53.0	7
Sodium hydroxide	0.30	15.0	2
Sodium carbonate	0.50	30.0	4
Sodium fluoride	0.18	7.5	1
Gum arabic	....	1.0	0.13
Corn sugar	....	7.5	1

This solution is 2 N in total cyanide and 0.3 N in total alkali, and may therefore be considered as consisting of 1.0 N $Na_2Zn(CN)_4$, with an excess of 0.3 N NaOH, in addition to the carbonate, fluoride, and other substances.

4. Methods of Analysis

In these solutions there is no difficulty in determining zinc. It is not possible, however, to titrate with even approximate

[1] *Trans. Am. Electrochem, Soc.*, vol. 40, p. 345, 1921.

accuracy the "free cyanide" or "free alkali." Approximate methods have been adapted to plating solutions[1] by C. M. Carson for the determination of total cyanide and alkali. Carbonate can be readily estimated.

(a) **Zinc.**—To 5 c.c. of the original solution add 5 c.c. each of concentrated nitric acid and concentrated sulphuric acid and evaporate the solution till dense white fumes appear. This evaporation must be conducted in a well-ventilated hood. After cooling the residue, add 3 c.c. of concentrated hydrochloric acid and 20 c.c. of water. The solution should then show no trace of blue color. If it does, add a few cubic centimeters of nitric acid and again evaporate the solution. Precipitate any iron and aluminum that may be present by the addition of ammonium hydroxide until the solution is just alkaline to litmus, and filter out and wash the precipitate, which may be used for the determination of iron and aluminum in the regular way. (Page 326).

Acidify the filtrate and determine the zinc in it by titration with potassium ferrocyanide, using uranium acetate as an outside indicator. Details of this titration are given on page 325.

(b) **Total Cyanide.**—Dilute a 25-c.c. sample of the solution to exactly 500 c.c. Dilute 25 c.c. of this solution to about 200 c.c. with distilled water, and add approximately 5 c.c. of 10 per cent sodium hydroxide solution and 1 c.c. of 10 per cent potassium iodide solution. Titrate the solution with tenth normal silver nitrate solution until a permanent faint yellow turbidity is produced. The solution should be stirred vigorously during the titration. Add a little more sodium hydroxide, and if the turbidity disappears, continue the titration with silver nitrate until a permanent turbidity is produced. One cubic centimeter of 0.1 N $AgNO_3$ = 0.0098 g. sodium cyanide (NaCN).

This titration gives the total cyanide, including that originally added both in the form of zinc cyanide and sodium cyanide. It is most convenient, however, to express the result as sodium cyanide, as will be illustrated in the subsequent examples. The results by this titration are not affected by the presence of aluminum salts or tartrates, but are too high in the presence of ammonium hydroxide. Addition of ammonium hydroxide, as frequently recommended for free cyanide titrations, should therefore be avoided.

[1] Bureau of Standards, *Tech. Paper 195.*

(c) Total Alkali.—The method which gives best results, which, however, are only approximate, is as follows:

Dilute 25 c.c. of the diluted solution (from b) to 200 c.c., and add slightly more than enough potassium ferrocyanide solution to precipitate the zinc, that is, slightly more than one-half of that required in (a), and slightly more silver nitrate than the amount required in (b). Then add a few drops of phenolphthalein solution, and titrate with standard (acid $N/5$ hydrochloric acid) until the pink color disappears for at least a few minutes.

By this method the total alkaline hydroxide plus one-half the carbonate is obtained. The amount of carbonate present may be separately determined by precipitation with barium chloride (page 231) and an appropriate correction made. Such a correction is necessary only if zinc carbonate or sodium carbonate has been added to the solution or if the solution has been in use for long periods. In most cases for control work the total alkali determined may be calculated as sodium hydroxide.

Example.—

(*a*) *Zinc.*—5 c.c. of the solution required 40 c.c. of a ferrocyanide solution, of which 1 c.c. = 0.005 g. zinc. Therefore $200 \times 40 \times 0.005 = 40$ g./l. zinc.

(*b*) *Total Cyanide.*—25 c.c. of the original solution was diluted to 500 c.c., and 25 c.c. of the diluted solution (that is, 1.25 c.c., or 1/800 l., of the original) was used in the titration with tenth normal silver nitrate (1 c.c. of which is equal to 0.0098 g. NaCN) and required 17 c.c. Therefore $17 \times 0.0098 \times 800 = 133$ g./l. sodium cyanide.

(*c*) *Total Hydroxide.*—For 25 c.c. of the diluted solution (that is, 1.25 c.c., or 1/800 l.) were added about 12 c.c. of the ferrocyanide solution and about 18 c.c. of silver nitrate, that is, slightly more of each solution than was required for the same amount of sample in the first two titrations. The solutions were then titrated, after the addition of phenolphthalein, with $N/5$ hydrochloric acid (1 c.c. of which is equal to 0.008 g. sodium hydroxide). It required 6 c.c. of hydrochloric acid. Therefore $6 \times 0.008 \times 800 = 38$ g./l. sodium hydroxide.

The solution therefore contained the following:

	N	g./l.	oz./gal.
Zinc	1.23	40	5.3
Total cyanide (Calc. as NaCN)	2.72	133	17.8
Total alkali (Calc. as NaOH)	0.95	38	5.1

The amounts of any given materials required to produce such a solution can be conveniently calculated from the normalities. Thus if the zinc is all to be added as zinc cyanide, it will require 1.23×59 (equiv. wt. of $Zn(CN)_2$) = 72 g./l. (9.7 oz./gal.) of $Zn(CN)_2$. In that case the NaCN in the solution will be $2.72 - 1.23 = 1.49$ N; therefore it will require $1.49 \times 49 = 73$ g./l.

(9.8 oz./gal.) of NaCN. The total amount, *viz.*, 38 g./l. (5.1 oz./gal.) of NaOH, would then be added.

If as large a part as possible of the zinc were to be added in the form of zinc oxide, this would be equivalent to the total alkali, *i.e.*, 0.95 *N*; 0.95 × 40.5 = 38.5 g./l. (5.1 oz./gal.) of ZnO. The remaining zinc, equivalent to 1.23 − 0.95 = 0.28 *N*, would be added as cyanide; therefore 0.28 × 59 = 16.1 g./l. (2.2 oz./gal.) of $Zn(CN)_2$. The sodium cyanide required would be 2.72 − 0.28 = 2.44 *N*, or 2.44 × 49 = 120 g./l. (16 oz./gal.). By the two methods of preparation, the solution would then require the following ingredients:

	N		g./l.		oz./gal.	
	1	2	1	2	1	2
Zinc cyanide	1.23	0.28	72	16	9.7	2.2
Zinc oxide	....	0.95	..	38	...	5.1
Sodium cyanide	1.49	2.44	73	120	9.8	16.0
Sodium hydroxide	0.95	....	38	...	5.1	

2. CADMIUM DEPOSITION

As previously noted, cadmium plating has been extensively applied in recent years. It is possible to deposit cadmium from slightly acid chloride or sulphate solutions, but the deposits are coarsely crystalline and entirely unsuited for electroplating unless some addition agents are present. In commercial plating the cyanide solution is usually employed.

Few formulas for cadmium plating solutions have been published.[1] They are ususally prepared by dissolving either cadmium cyanide, $Cd(CN)_2$, or cadmium oxide (CdO) in sodium cyanide. In both cases the solution contains "free cyanide" and the double cyanide $Cd(CN)_2.NaCN$ or $NaCd(CN)_3$; and if cadmium oxide is used the solution also contains free sodium hydroxide.

$$CdO + 3NaCN + H_2O = NaCd(CN)_3 + 2NaOH$$

Unlike with zinc solutions, the sodium hydroxide does not combine with cadmium to form soluble compounds.

The concentrations may vary appreciably according to the conditions of operation to be employed. Thus the cadmium content may vary from 15 to 30 g./l. (2 to 4 oz./gal.), *i.e.*, from 0.25 to 0.8 *N*; and the free sodium cyanide from 7.5 to 30 g./l. (1 to 4 oz./gal.), *i.e.*, from 0.15 to 0.6 *N*. A typical solution

[1] Information regarding methods of cadmium plating is contained in articles by E. Blassett (*Metal Ind.*, vol. 9, p. 509, 1911); C. M. Hoff (*Trans. Am. Electrochem. Soc.*, vol. 50, p. 301, 1926); by C. H. Loven (*Metal Ind.*, vol. 26, p. 252, 1928); and by L. P. Westbrook (*Trans. Am. Electrochem. Soc.*, vol. 55, p. 333, 1929).

with the same composition may be prepared according to either of the following formulas:

(*a*)	*N*	g./l.	oz./gal.
Cadmium oxide (CdO).....	0.5	32	4.2
Sodium cyanide (NaCN).....	1.5	75	10

or

(*b*)			
Cadmium cyanide, $Cd(CN)_2$.....	0.5	41	5.5
Sodium cyanide (NaCN).....	1.0	49	6.5
Sodium hydroxide (NaOH).....	0.5	20	2.7

Such a solution is 0.5 *N* in $NaCd(CN)_3$, 0.75 *N* in free NaCN, and 0.5 *N* in free NaOH.

Some baths contain ammonium hydroxide either added as such, or formed in the solution by the addition of ammonium sulphate and sodium hydroxide. Addition agents are usually employed to produce brighter deposits. Among those suggested are glue, casein, wood pulp extract (gulac) and turkon oil (sulphonated castor oil). Westbrook found small amounts of nickel to be beneficial.

The solution is operated under conditions similar to those with the zinc cyanide solution; *i.e.*, at ordinary or slightly elevated temperatures, and at current densities from 1 to 5 amp./dm.^{2} (9 to 47 amp./sq. ft.). The anodes are sometimes made up of both cadmium and steel, the relative areas of which are adjusted by various means. Pure cadmium anodes can be used however.

Methods of analysis of cadmium solutions are very similar to those for zinc, although the cadmium itself is usually determined not volumetrically but gravimetrically as oxide or sulphide. It can be titrated by the ferrocyanide method as used for zinc, in which case any zinc also present in the solution is included in the titration.

Cadmium can be stripped quantitatively with hydrochloric acid containing antimony chloride, under the same conditions used for stripping zinc.

CHAPTER XVIII

LEAD AND TIN DEPOSITION

Lead and tin are similar in many chemical and electrochemical properties. Both of them are less subject to corrosion than zinc or cadmium. Lead owes its use chiefly to its resistance to the action of sulphuric acid, while tin is employed largely because of its ability to withstand organic acids, such as those present in foods. Lead is, however, readily attacked by certain organic acids and tin is easily dissolved by sulphuric acid. As both of these metals are below iron in the electrochemical series, they do not offer intrinsic protection to the iron; hence the latter is attacked if exposed by porosity or abrasion, and corrosion may be appreciably accelerated by the presence of the lead or tin. It is therefore more important to secure impermeable coatings of these metals than it is of zinc.

Neither of these metals has been applied electrolytically to a great extent, owing to the fact that they melt readily and coatings can be more easily produced by hot dipping than by electrodeposition. It is not feasible to secure adhesion of pure molten lead to steel, and therefore a small amount (usually 10 to 20 per cent) of tin is mixed with the lead. The resulting coated metal is known as "terne plate" and is used extensively for roofing, etc. When a layer of pure lead is required this may be secured by first coating the steel with terne plate and then applying a layer of pure lead. Mercury is also used to secure the adherence of molten lead. The future application of lead plating depends largely upon its use in those cases where pure coatings are essential and where it is not feasible to apply them by the hot-dipping method or by the use of sheet lead.

Hot-dipped tin coatings are most extensively applied and have thus far yielded more satisfactory service than electroplated coatings, especially upon kitchen utensils, where heavy coatings are required both upon the inside and outside. Electroplating with tin has been applied principally to those classes of work upon which a heavy coating is not necessary. In recent years

however there has been a marked increase in the application of fairly thick deposits, *e.g.* upon coils and other parts of domestic refrigerators. Much of the tin plating now used is plating by immersion, which produces, at best, very thin coatings.

1. LEAD DEPOSITION

Lead can be deposited from a great variety of solutions, including the acidified solutions of the nitrate, acetate, lactate, perchlorate, fluosilicate, and fluoborate, and alkaline plumbates or double cyanides. Actually, however, dense deposits, suitable for plating, cannot readily be produced from many of these solutions and in practice only the fluosilicate, fluoborate, and perchlorate baths are employed. The other acid solutions all show a marked tendency for the formation of treed or spongy deposits, while in the alkaline solutions it is difficult to secure adequate anode corrosion.

Although lead had been previously deposited from both fluosilicate and fluoborate solutions, these were never applied commercially until Betts[1] developed their operation with addition agents, such as glue, etc. The fluosilicate was then used for lead refining, and to a slight extent for lead plating of storage battery fittings. During the Great War lead plating was extensively applied. At first the fluosilicate solution, as used in and purchased from lead refineries, was employed, and entirely satisfactory deposits were secured. Subsequently the fluoborate solution was quite extensively used because (*a*) it can be produced on a small scale more conveniently from commercially available materials; (*b*) it can be used for plating directly upon steel, whereas with the fluosilicate bath preliminary coating with copper is necessary; (*c*) the fluoborate solutions are more stable, *i.e.*, decompose less rapidly during use; and (*d*) the deposits from the fluoborate are slightly finer grained than from the fluosilicate. On the other hand, the fluosilicate solution can be produced more cheaply, especially upon a larger scale.

1. Fluosilicate Solution

Fluosilicic acid (H_2SiF_6) is produced by the action of hydrofluoric acid (HF) upon silica (SiO_2) in the form of sand or powdered quartz

$$SiO_2 + 6HF = H_2SiF_6 + 2H_2O$$

[1] Betts, A. G., "Lead Refining by Electrolysis," Wiley & Sons, 1908.

When basic lead carbonate, commercial "white lead," $Pb(OH)_2.2PbCO_3$, is dissolved in fluosilicic acid, lead fluosilicate, $PbSiF_6$, is formed. An excess of the acid is always found beneficial, owing, no doubt, to the fact that it improves the conductivity and decreases the lead ion concentration.

Although it is possible to secure thin deposits of lead, which are also smooth and dense, from either fluoborate or fluosilicate solutions at low current densities, higher current densities produce coarse, treed deposits, especially if deposition is continued for some time. Almost invariably, therefore, addition agents are employed. Various substances have been suggested, but those most frequently employed are colloids, such as glue or gelatin, or reducing sugars, added as such or in the form of molasses, which is subsequently inverted to reducing sugars in the acid solutions. The function of these substances is similar to that in other plating solutions, but the effects are very much more marked, especially with respect to treeing or roughness.

The fluosilicate bath recommended by Betts contains 8 per cent of Pb and 15 to 16 per cent of SiF_6. If we assume that by "per cent" is meant grams per 100 c.c., this is equivalent to 80 g./l. of Pb and 150 to 160 g./l. of SiF_6, *i.e.*, the solution is about 0.8 *N* in lead, and about 2 *N* in total fluosilicate radical, in which case the "free" fluosilicic acid would be about 1.2 *N*. The proportions of lead and free acid used may vary over wide limits and still permit the production of good deposits. Thus, *e.g.*, A. G. Reeve[1] used, for plating shells, a fluosilicate solution which contained 18 per cent of lead and 14 per cent of fluosilicic acid, equivalent, therefore, to about 1.75 *N* in lead and 2 *N* in total acid; or with only 0.25 *N* free acid. The free acid actually determined by Reeve in such a solution was 2.9 per cent, *i.e.*, about 0.4 *N*. It is not feasible to prepare the fluosilicic acid upon a small scale, so the plating solution is usually purchased from the lead refineries. In addition to glue, molasses or other sugars are often employed (usually about 1 part in 5,000).

2. Fluoborate Solutions

Fluoboric acid (HBF_4) is produced by mixing hydrofluoric acid and boric acids:

$$H_3BO_3 + 4HF = HBF_4 + 3H_2O$$

[1] *Trans. Am. Electrochem. Soc.*, vol. 36, p. 161, 1919.

It is probable that the formula of fluoboric acid is much more complex, but for convenience the formula HBF_4 is employed. It is at least known that in a mixture of hydrofluoric and boric acids some more complex acids are formed. The term "fluoboric acid" is usually applied to this somewhat indefinite product of the union of the two acids. If basic lead carbonate is dissolved in fluoboric acid, we may assume that lead fluoborate, $Pb(BF_4)_2$, is produced. In such solutions an excess of the acid is employed, for the same reasons as above stated.

The studies on fluoborate solutions at the Bureau of Standards[1] indicated that satisfactory thin deposits can be obtained when the lead content of the solution is N and the total fluoboric acid (calculated as HBF_4) is 1.5 N. For thick deposits or rapid deposition, solutions of twice this concentration can be employed. The preparation of the normal solution from commercial materials will require the following amounts:

	g./l.	oz./gal.
Basic lead carbonate, $Pb(OH)_2.2PbCO_3$.	150	20
50 per cent hydrofluoric acid (HF).....	240	32
Boric acid (H_3BO_3).....	105.	14
Glue.....	0.2	0.025

The specific gravity = approximately 1.17, or 21°Bé. This formula is based upon the arbitrary assumption that the commercial 48 to 52 per cent hydrofluoric acid contains about 2 per cent of sulphuric acid, the average content found in a number of samples tested. This precipitates part of the lead as lead sulphate ($PbSO_4$), and hence a correspondingly greater amount of the lead carbonate must be used.

In preparing this solution, the hydrofluoric acid is first placed in a lead-lined or rubber-lined tank and the boric acid crystals are added in small amounts while the mixture is stirred with a wooden paddle. After all the boric acid is added, the solution is allowed to cool, after which the lead carbonate is added slowly in the form of a thin paste with water. As effervescence results from the solution of the lead carbonate and the evolution of carbon dioxide, it is necessary to use care to prevent the solution from foaming over. When all the lead carbonate has been added, the precipitate of lead sulphate is allowed to settle, and the clear solution is then siphoned or filtered in the plating tank, which

[1] Blum, W., Liscomb, F. J., Jencks, Z., and Bailey, W. E., *Trans. Am. Electrochem. Soc.*, vol. 36, p. 243, 1919.

may be wood or stoneware, preferably lined with asphalt. The glue is then added in the form of a solution in warm water and the bath is diluted to the desired volume or specific gravity.

It has been found most satisfactory to employ a current density of 1 to 2 amp./dm.^{2} (9.3 to 19 amp./sq. ft.), but with good agitation, especially in the more concentrated solution, good deposits can be secured at 3 amp./dm.^{2} (28 amp./sq. ft.). For this and other lead solutions agitation is found very helpful, if secured by mechanical means, such as the rotation of the anode or of a wooden paddle. Air agitation is, however, entirely unsatisfactory in lead plating, probably because the lead is so readily oxidized, and hence there is occlusion of oxides or basic salts.

In this and other lead baths it is found that the best adherence of the deposit can be secured if the surface of the steel is cleaned by sand-blasting rather than by pickling. As previously noted, there is a tendency for the absorption of hydrogen by the steel during pickling, and this may cause peeling of the lead deposit, especially if, as is sometimes necessary, the plated metal is subsequently heated to fairly high temperatures but below the melting point of lead. Whatever method of cleaning is employed, it is absolutely essential that the surface be entirely free from slag or oxides if the lead coating is to be impervious, which it must be for securing satisfactory protection of the steel.

3. Perchlorate Solutions

The perchlorate solution is formed by the solution of basic lead carbonate in perchloric acid ($HClO_4$). This acid is made by treatment of sodium or potassium perchlorate with sulphuric acid, and distillation under reduced pressure. When properly prepared, the acid is quite stable, but as it is relatively expensive it has not been used extensively. Some fear has been expressed regarding the danger of explosion of perchlorates if mixed with organic materials, such as paper, wood, etc. It is well known that chlorates, *e.g.*, $NaClO_3$ or $KClO_3$, form dangerous mixtures with organic materials. The perchlorates are, however, much more stable and so far as known have never caused explosions under conditions such as may arise in a plating plant.

The perchlorate bath as recommended by Mathers[1] contains 5 to 6 per cent of lead, 2 to 5 per cent of perchloric acid, and 0.05

[1] *Trans. Am. Electrochem. Soc.*, vol. 23, p. 159, 1913.

per cent of peptone or clove oil. A bath containing 6 per cent (60 g./l.) of lead and 4 per cent (40 g./l.) of free perchloric acid is about 0.56 *N* in lead and 0.4 *N* in free acid. This solution also gives good deposits over a wide range of composition. A current density of 2 to 3 amp./dm.^{2} (19 to 27 amp./sq.ft.) is employed.

4. Tests of Coatings

As lead coatings are useful especially for securing resistance to the attack of sulphuric acid or similar corrosive agencies (*e.g.*, on storage battery fittings), it is important that they should be impervious. The addition agents recommended for the various baths all tend to produce dense deposits and freedom from porosity. It is not usually possible, however, to secure impervious deposits of lead unless the coating is considerably thicker than that used for nickel, zinc, or other metals. Under favorable conditions, deposits 0.075 mm. (0.003 in.) thick will usually be impervious, though for many purposes thicker deposits may be justified. Fortunately, the electrochemical equivalent of lead is high, and hence it is possible to deposit a coating of 0.075 mm. (0.003 in.) in about 1 hr. if a current density of 2 amp./dm.^{2} (19 amp./sq. ft.) is employed.

It is possible to test the lead coatings for porosity without injuring them, by using a simple modification of the well-known "ferroxyl" test (p. 131). If a solution containing about 10 g./l. (1.5 oz./gal.) of potassium ferricyanide, $K_3Fe(CN)_6$, and 20 g./l. (3 oz./gal.) of sulphuric acid is applied to lead-coated steel, a blue spot will be produced, usually in less than a minute, if the steel is exposed at any point. This blue color (Turnbull's blue) is formed by reaction between the ferrous sulphate (which is formed if any iron is dissolved by the sulphuric acid) and the ferricyanide. If slight porosity of the lead coating is indicated by such a test, the surface may be rendered impervious by a slight burnishing action produced by steel balls or other simple means.

5. Analysis of the Solutions

In all of the above solutions lead may be readily determined by precipitation with sulphuric acid. A 10-c.c. sample of the solution is diluted to 150 c.c., heated nearly to boiling, and a slight excess of dilute sulphuric acid is added. The precipitate of lead sulphate is allowed to settle and is then filtered out on

a weighed Gooch crucible, washed with very dilute sulphuric acid and finally with water, and is then dried and weighed as $PbSO_4$. From this weight the content of metallic lead, or lead fluosilicate, fluoborate, or perchlorate may be readily calculated.

The free fluosilicic acid may be approximately determined by titrating with potassium hydroxide using phenolphthalein as the indicator. In other methods the fluosilicic acid is precipitated as K_2SiF_6 by the addition of an alcoholic solution of potassium acetate, and the precipitate is dissolved and titrated hot with sodium hydroxide. The results by either method are useful only for comparative analyses of the same bath. The fluoboric acid is still more difficult to determine by titration, and no satisfactory method of analysis has been devised. The free perchloric acid can be determined by direct titration, or, more accurately, by precipitating the lead with a calculated excess of sulphuric acid and titrating in the filtrate the total acid; from this the free acid originally present may be calculated.

2. TIN PLATING

As previously noted, until in recent years tin plating has not been practiced to a very great extent in this country, owing to the ease with which tin can be applied by hot dipping and the difficulties of securing dense, impervious deposits by electrodeposition. In the absence of addition agents, tin shows a very marked tendency to produce treed or spongy deposits. This defect has been sufficiently overcome to permit electrolytic tin refining to be carried out successfully, but the deposits have not thus far competed with hot tin for the production of protective coatings. Most of the studies upon tin refining have been directed toward the discovery of satisfactory addition agents. According to Kern's experiments,[1] stannous fluosilicate solutions containing aloin gave the best deposits. A recently patented bath consisting of an acidified solution of sodium sulphate and stannous sulphate with aloin as an addition agent is employed commercially for tin refining and may prove suitable for electroplating.

1. Electrolytic Processes

In all cases the tin is probably deposited from solutions containing the metal in the stannous condition (Sn^{II}). If stannic salts

[1] *Trans. Am. Electrochem. Soc.*, vol. 33, p. 145, 1918.

(Sn^{IV}) are electrolyzed with tin anodes the tin is reduced almost completely to the stannous form. One difficulty of securing good tin plating baths is that of securing suitable stannous compounds. The simplest commercial stannous compound is the chloride ($SnCl_2.2H_2O$); a common stannic salt is sodium stannate (Na_2SnO_3), which must be reduced before tin is deposited. If it is desired to prepare solutions such as the fluoborate or fluosilicate, it is necessary to precipitate stannous hydroxide by the addition of alkali to stannous chloride, and to dissolve this precipitate in the desired acid. Tin is not readily dissolved by acids except hydrochloric and therefore the direct production of such salts is not practicable. Fairly dense, thin deposits of tin can be obtained from fluoborate solutions containing glue. Such solutions have not been applied, however, partly because of the difficulty of preparing stannous fluoborate.

Among the tin plating baths that have found appreciable application in this country are the alkaline baths, containing sodium stannite (Na_2SnO_2) with an excess of alkali. Usually an addition agent is present, and in some cases cyanide is added. A bath which was applied successfully during the war had the following composition:

(1)

	N	g./l.	oz./gal.
Stannous chloride ($SnCl_2.2H_2O$)	0.25	30	4
Sodium hydroxide (NaOH)....	1.80	75	10
Glucose (dextrose, $C_6H_{12}O_6$)....	....	60	8

We may assume that such a solution is 0.25 *N* in sodium stannite and about 1.3 *N* in free alkali and 0.25 *N* in sodium chloride. It requires one equivalent of NaOH to precipitate the stannous hydroxide, and one to redissolve it to form sodium stannite.

$$SnCl_2 + 2NaOH = Sn(OH)_2 + 2NaCl$$
$$2NaOH + Sn(OH)_2 = Na_2SnO_2 + 2H_2O$$

The dextrose, or mixture of dextrose and dextrin if corn syrup is used, is a very essential and very efficient addition agent in such baths. This solution is operated at about 50°C. (122°F.) at a current density of about 1 amp./dm.^{2} (9 amp./sq. ft.).

More recently, solutions prepared from sodium stannate (Na_2SnO_3) have been employed. In them the tin has a valence of four, while in stannite it has a valence of two. Only half as much tin is deposited by a given current from stannate as from

stannite. A typical formula proposed by W. Fraine[1] is as follows:

(2)

	N	g./l.	oz./gal.
Sodium stannate (Na_2SnO_3).....	1.8	180	24
Stannous chloride ($SnCl_2.2H_2O$)....	0.02	2	0.25
Rosin (dissolved in NaOH).....	....	0.2	0.03

Such a solution is used at a temperature of about 60°C. (140°F.), at a current density of about 0.5 to 1 amp./dm.^{2} (5 to 9 amp./sq. ft.). It is at least probable that during operation with tin anodes a large part of the stannate is reduced to stannite. In some cases it has been found advantageous to add sulphurous acid (H_2SO_3) to reduce the stannate.

2. Contact and Immersion Processes

Even though electrolytic tin plating was not extensively applied till recently, large quantities of small articles, such as pins, safety pins, thimbles, buttons, etc., are coated with tin by the contact or immersion processes, which are, strictly speaking, electrolytic, though the current is furnished within the tank instead of from an outside source. On all such work the coatings are very thin, but very fine-grained and bright, and unlike most deposits produced by immersion they are very adherent. This is partly due to the fact that in all of the solutions used the tin ion concentration is very low, and hence the rate of deposition is slow and treeing is prevented. The production of dense impervious deposits is aided by the relatively high overvoltage of hydrogen on tin. In those immersion processes which depend upon the electrolytic action of the base metal, deposition necessarily stops as soon as the base metal is entirely covered; hence only very thin deposits are secured.

In one of the simplest methods the brass articles to be tinned are rotated for 2 to 4 hr. at a temperature of 80°C. (176°F.) in a barrel containing the solution and small pieces of zinc. The solution consists of:

(1)

	N	g./l.	oz./gal.
Tin (stannous) chloride ($SnCl_2.2H_2O$)....	0.20	25	3.5
Cream of tartar (potassium acid tartrate, $KHC_4H_4O_6$).....	0.12	10	1.3

[1] *Monthly Rev. Am. Electroplaters Soc.*, vol. 13, No. 8, Aug. 1926.

If pieces of brass and of zinc are in contact in such a solution, a cell is produced in which the zinc becomes the anode, *i.e.*, passes into solution, and the brass becomes the cathode, *i.e.*, is coated with the tin. One function of the acid tartrate is to form, to some extent at least, complex ions, which produce a small concentration of stannous ions, and which do not readily hydrolyze or precipitate stannous hydroxide.

In a somewhat similar method known as the "cream of tartar immersion process" the solution consists of:

(2)

	N	g./l.	oz./gal.
Cream of tartar (potassium acid tartrate, $KHC_4H_4O_6$).....	0.015	1.5	0.2
Sodium chloride (NaCl).....	0.05	3.0	0.4

The brass objects are placed in thin layers on iron wire trays, covered with perforated sheets of pure tin, in the solution which is heated by steam coils in a copper tank to a temperature of at least 90°C. (194°F.) for 3 to 5 hr. In this case the tin gradually passes into solution, but at no time reaches a high concentration, as it is soon plated out upon the brass, the potential of which is similar to that of copper, *i.e.*, is below tin in the electromotive series. A fresh solution is used for each batch of work, and is removed quickly in order to permit rapid rinsing and drying of the parts.

For coating brass with tin by immersion, alkaline solutions are also employed. Such a solution, for example, may contain:

(3)

	N	g./l.	oz./gal.
Stannous chloride ($SnCl_2.2H_2O$).	0.25	30	4
Sodium hydroxide (NaOH).....	1.50	60	8

The brass articles to be plated are placed in an iron tank on iron wire trays covered with perforated sheets of tin in the solution which is heated to 90°C. (194°F.) for 2 to 3 hr. In this process the tin becomes the anode and passes into solution and is deposited upon the brass. For some articles more dilute solutions are used.

Iron and steel articles are tinned by being placed in thin layers on iron wire trays covered with perforated zinc sheets, in a galvanized iron vessel. The articles are kept for about 45 min. in a solution which has been heated nearly to boiling, but is not subsequently heated. The solution is discarded each time and

the articles are quickly rinsed and dried. A typical solution is as follows:

(4)

	N	g./l.	oz./gal.
Stannous chloride ($SnCl_2.2H_2O$)....	0.13	15	2
Sodium sulphate ($Na_2SO_4.10H_2O$)...	1.0	160	21

In preparing this solution it is customary to dissolve the required amounts of the above salts in about one third of the final volume of hot water, and to add this solution to the remaining two thirds of the hot water, which has been placed in the iron tank containing the articles to be plated. A little hydrochloric acid is then added, *e.g.*, about one drop to each gallon of solution. The probable function of the sodium sulphate is to increase the conductivity.

3. Analysis of Solutions

In acid solutions which are in contact with metallic tin, we may assume that practically all of the tin is in the stannous condition. In the absence of organic reducing agents, such as tartrates, the tin content can be very quickly determined by adding an acidified solution of ferric sulphate (or chloride) and titrating the resultant ferrous salt with permanganate. If much hydrochloric acid is present, the manganous sulphate titrating mixture may be added.

The alkaline tin solutions must be acidified with hydrochloric acid, and if cyanides are present, are boiled till they are expelled. The tin may then be precipitated with hydrogen sulphide, and determined by ignition to stannic oxide, or by solution, reduction, and titration with iodine solution. The acid tin solutions containing tartrates may be precipitated directly with hydrogen sulphide.

CHAPTER XIX

SILVER DEPOSITION

Silver plating is extensively used for ornamental purposes because of its white color and high luster. Its use on tableware, especially "flatware," such as knives, forks, and spoons, depends upon the fact that silver is not readily attacked or dissolved by organic acids or most other constituents of foods. Silver is not oxidized on exposure to air, but is readily tarnished by sulphides, such as the hydrogen sulphide that may enter the air from coal stoves or from illuminating gas, or the sulphides present in certain foods, such as eggs, mustard, etc. If the silver or silver plated articles are principally for ornamental purposes, they should be lacquered whenever possible. As this is not practicable upon tableware, it is necessary to remove the sulphide from the surface at intervals either by mechanical polishing or by the "electrolytic" cleaning method. In this, the silverware is immersed and heated in a dilute solution of sodium bicarbonate ($NaHCO_3$) and sodium chloride (NaCl) in contact with a sheet of aluminum or zinc. The base metal becomes the anode of the cell thus formed and passes into solution. The silver sulphide is reduced upon the surface of the silver, which forms the cathode, and the sulphur is removed with almost no loss of silver.

Silver is sometimes deposited upon metals by immersion, or by rubbing solutions or pastes containing silver compounds, upon the metal surface. Such processes produce very thin films, which have little value for wear resistance. Many such materials contain cyanides or mercury, and should not therefore be used by novices, or for domestic purposes. A simple safe mixture may be prepared from 2 parts of silver nitrate, 1 of ammonium chloride, 4 of sodium thiosulphate (hypo), and 4 of calcium carbonate. These are mixed with water to form a paste, which is then rubbed on the metal surface.

1. COMPOSITION OF BATHS

All silver plating is conducted in cyanide solutions, not because it is not possible to deposit silver from simple salt solutions, but

because (*a*) the metals to be plated would precipitate the silver from its ordinary salts, and (*b*) silver deposited from such salts as the nitrate or acetate is usually in very coarse crystals. The cyanide silver solution may be prepared by dissolving silver cyanide in sodium or potassium cyanide, forming a double cyanide:

$$AgCN + KCN = KAg(CN)_2$$

Formerly potassium cyanide was used exclusively for this purpose, but during the war it was almost completely displaced by the sodium salt (page 220). It is now believed by most platers that potassium cyanide gives better results in silver plating. One objection to the sodium cyanide is that the sodium carbonate formed in the solution is less soluble than the corresponding potassium carbonate.[1] Another advantage of the potassium compounds is that their conductivity (in equivalent solutions) is about 60 per cent more than that of the sodium salts.[2]

F. C. Mesle[3] found that the deposits from potassium cyanide baths burnish more easily than those from sodium cyanide.

It is also possible to prepare the solution by dissolving silver chloride (AgCl) in potassium cyanide, in which case an equivalent amount of potassium chloride is produced and remains in the solution:

$$AgCl + 2KCN = KAg(CN)_2 + KCl$$

Whether the potassium chloride is beneficial or not has not been definitely determined, but at least it is not seriously detrimental. When the chloride is used, it requires twice as much potassium cyanide to produce the double cyanide.

In any case it is customary to have in the solutions an appreciable excess of potassium cyanide, usually known as "*free cyanide.*" The free cyanide includes all the alkali cyanide above that required to form the double cyanide, *i.e.*, above the one equivalent if silver cyanide has been used, or above two equivalents if silver chloride has been dissolved. It is possible also to dissolve silver oxide (Ag_2O) in cyanide, in which case the solution will contain free potassium hydroxide:

$$Ag_2O + 4KCN + H_2O = 2KAg(CN)_2 + 2KOH$$

[1] Hogaboom, G. B., *Jour. Electroplaters' & Depositers' Tech. Soc.*, vol. 3, p. 73, 1928.

[2] Sanigar, E. B., *Trans. Far. Soc.*, vol. 24, p. 45, 1928.

[3] *Monthly Rev. Am. Electroplaters' Soc.* vol. 15, no. 10, p. 4, 1928.

This method of preparation is not, however, extensively used. The plating solutions invariably contain carbonate (*e.g.* K_2CO_3), especially after they have been in use for some time. This is produced by decomposition or oxidation of the cyanide (page 223). Formerly it was believed that the carbonate was detrimental in the solutions. In recent years, however, it has been claimed that up to certain limits it may actually be beneficial, provided that the free cyanide content is also high.

The methods for plating different metals with silver vary principally in the preliminary treatment of the metals. Thus iron or steel is usually plated first for a few seconds in a very weak "*strike*" containing a very small amount of silver, some copper, and a large amount of free cyanide. It is then plated in a second strike containing little silver and much free cyanide, and finally in the regular silver solution. Copper and brass are first coated with mercury by immersion in a solution of mercuric chloride, the so-called "*blue dip*," or in mercuric cyanide, and are then given a "strike" and plated in the regular way. Nickel alloys such as "nickel silver" (German silver) can be plated without using a mercury dip.

The solution used for the final silver plating of any of these metals is referred to as the plating solution. It contains usually from 15 to 30 g./l. (1.8 to 3.6 troy oz./gal.) of metallic silver, *i.e.*, it is from about 0.15 to 0.3 *N* in metal. The free cyanide may vary considerably, being usually, however, from 50 to 100 per cent of the combined cyanide. For "hollow ware" the free cyanide is usually higher than for flatware, *e.g.*, up to 200 per cent of the combined cyanide. The excess cyanide probably increases the throwing power.[1] The free cyanide may be conveniently calculated in terms of normality. If, *e.g.*, a solution is 0.25 *N* in silver, the combined cyanide must be 0.5 *N*, as it requires two equivalents of cyanide to one of silver to form the double salt, $KAg(CN)_2$. In such a solution, therefore, the free cyanide would usually be from 0.25 to 0.5 *N*, *i.e.*, from 16 to 32 g./l. (2.1 to 4.2 oz./gal.) of potassium cyanide. The higher concentration of free cyanide is especially desirable in old solutions, of which the carbonate content is high. It is probable that in such solutions the high cyanide is advantageous in

[1] GLASSTONE, S., (*Jour. Chem. Soc.*, p. 690, 1929) found that a large excess of cyanide makes the polarization curve more vertical, which corresponds to a decrease in throwing power.

aiding anode corrosion, which in the presence of carbonate may be poor.

Silver deposited from the regular cyanide solutions, such as just described, is rather coarsely crystalline with a white frosted appearance. Buffing or burnishing is therefore necessary to secure a bright surface. It is possible to produce bright silver deposits from solutions containing very small amounts of carbon disulphide (CS_2), which serves as a "*brightener*." Even such "bright deposits" usually require "coloring" to secure a satisfactory finish. Carbon disulphide is the only addition agent commonly employed in silver solutions. No clear explanation of its effect has ever been made. It seems most probable that the carbon disulphide is either dissolved or in suspension in the solution, forming in the latter case a very fine emulsion. That it is not chemically combined, at least in any stable compound, is shown by the fact that it gradually evaporates from the solution, and if at any time an excessive amount is added (as indicated by a dark deposit) it is possible to eliminate it by warming or by blowing air through the solution. The bright deposits of silver are reported to contain traces of sulphur, but whether this is present as silver sulphide or as an organic sulphide has not been determined. That the brightening effect is due principally to a decrease in crystal size is evident not only from the appearance of the deposit when slightly magnified, but also from the greater density of the bright deposit. It is well known that a deposit of a given weight of silver produced from a "bright bath" is decidedly thinner than one of the same weight produced from the regular bath.

H. E. Haring[1] found that, unlike most addition agents, the carbon disulphide decreases the cathode polarization. S. C. Langdon[2] confirmed this observation, but also found that if the electrolysis is conducted in the absence of air, the disulphide increases the cathode polarization. The subject evidently needs further investigation.

2. POTENTIALS INVOLVED

In order to understand the solutions and methods used in silver plating, it is necessary to recall its position in the electrochemical series (Table 10, Appendix). The fact that most of the metals are far above silver, and therefore tend to precipitate it

[1] *Trans. Am. Electrochem. Soc.*, vol. 49, p. 417, 1926.

[2] Private communication.

from its solutions, makes difficult the plating of such metals with adherent coatings of silver. The treatment required for any metal depends upon the potential of that metal in the silver solution. This in turn depends upon the composition and silver ion concentration of the solution.

The most complete study of the potentials of various metals in silver solutions was made by Frary and Porter[1] in 1915. The little consideration given to the paper in this country by commercial platers or chemists is a good illustration of the need for a coordination of the results of research and practice. All of their experiments were made with solutions containing potassium silver cyanide, $KAg(CN)_2$, but it appears reasonably certain that the same conclusions will apply at least qualitatively to the corresponding sodium salts, prepared with sodium instead of potassium cyanide. All of their values were expressed in terms of potentials and referred to the absolute zero of potential, which is -0.277 volt with respect to the hydrogen electrode, which latter is considered as the zero of reference in this text. Wherever potentials are here quoted from Frary and Porter, they have been revised by deducting 0.277 volt.

The above authors measured the potentials of silver, mercury, copper, brass, iron, and zinc in silver solutions containing definite concentrations of potassium silver cyanide, free potassium cyanide, potassium chloride, and potassium hydroxide, all of which (or the corresponding sodium salts) may be present in silver plating solutions. No tests were made, however, with solutions containing carbonates. Their results were shown in the form of tables and curves, from which the following conclusions may be drawn.

The potential of silver is chiefly of interest as indicating the probable silver ion concentration of the solutions. With 0.25 N silver solutions (containing 27 g./l., or 3.2 troy oz./gal., of metallic silver) the potential of silver decreases from $+0.150$ volt when no free cyanide is present to -0.217 volt when the free cyanide is 0.025 N (*i.e.*, 1.6 g./l., or 0.2 oz./gal., of KCN), and to -0.369 volt when the free cyanide is 0.25 N (*i.e.*, 16 g./l., or 2.1 oz./gal., of KCN). These potentials correspond respectively to silver ion concentrations of about 10^{-11}, 10^{-17}, and 10^{-20} N. Even the solution with no free cyanide has a very low metal ion concentration, which is characteristic of complex cyanide solutions, but the addition of free cyanide reduces

[1] *Trans. Am. Electrochem. Soc.*, vol. 28, p. 307, 1915.

the silver ion concentration very greatly. It was found that mere dilution of the silver cyanide solutions, especially those with little or no free cyanide, actually increases slightly their silver ion concentration. This observation indicates that the dissociation of the complex metal cyanides is more complicated than has usually been assumed. At least it is of importance to note that the way to decrease the silver ion concentration and thus to prevent deposition by immersion is not to dilute the solution but to increase the free cyanide content. In this fact is to be found the explanation of the use of a silver "strike" high in free cyanide content for initial plating upon many metals. From a solution of a simple silver salt such as silver nitrate, with a high concentration of silver ions, or even from a cyanide silver solution containing no free cyanide, the iron or steel can readily deposit silver by immersion, but from solutions with much free cyanide and hence low silver ion concentration, no such deposition occurs. This explanation is confirmed by the fact that in the solutions containing no free cyanide the potential of the iron was found to be negative to the silver (*i.e.*, it is able to throw silver out of the solution), while in those containing free cyanide the relative potential of iron is reversed, *i.e.*, it becomes positive to the silver, and hence cannot displace it.

Copper and brass have nearly the same potentials in most silver solutions, although the brass tends to be more negative, especially when first immersed, showing that the zinc in the brass has some effect on its potential. In almost all the solutions tested, copper and brass have potentials more negative than silver, *i.e.*, they tend to deposit silver by immersion. Mercury, on the other hand, has a positive potential toward silver in all solutions containing free cyanide. If, therefore, either copper or brass is immersed in a mercuric cyanide solution, there will be precipitated upon the surface a film of mercury; and if the object is then placed in a silver solution (containing free cyanide), there is no tendency for deposition of the silver by immersion, and hence an adherent deposit of silver is secured. At first it might appear preferable to deposit upon the copper a metal intermediate in potential between it and the silver, if such a metal were available, rather than one, such as mercury, the potential of which in such solutions is on the other side of silver. That the deposit of mercury produced on copper by immersion

is adherent while that of silver is not, in spite of the fact that there is a greater difference in potential between the copper and mercury than between the copper and silver, is due probably to the very decided tendency of the mercury to alloy or amalgamate with the copper or brass. The mercury may also produce increased adhesion of the subsequently deposited silver by alloying with it, although an excess of mercury will decrease the adhesion. Another advantage of the mercury film is that it protects the copper or brass from oxidation during the transfer to the silver bath. A disadvantage of the mercury dip is that it accelerates "season cracking" of brass.

No measurements were made by Frary and Porter of the single potentials of nickel, lead, or tin, or alloys containing them, but from the position of these elements in the electromotive series it seems at least probable that their potentials are intermediate between those of copper and of iron. This prediction is confirmed by the customary method of plating them in a preliminary strike, though occasionally the mercury dip is used on the lead-tin alloys. In either method, deposition of silver by immersion is prevented. In recent years brass is frequently plated with nickel prior to silver plating. Attempts to measure the potential of zinc in these solutions were not very successful, due to the immediate deposition of silver by immersion. The results showed, however, that zinc is decidedly negative to silver in practically all of these solutions. This observation is also in accord with commercial procedure, in which it has been found impracticable to silver plate zinc, or alloys high in zinc, without a preliminary coating of nickel, or of copper from the cyanide bath. Alloys high in lead are usually copper plated before silvering.

3. FUNCTIONS OF CONSTITUENTS IN BATHS

The functions of the principal constituents of the silver bath are fairly well defined. The metal content is furnished entirely by the double silver cyanide, $NaAg(CN)_2$ or $KAg(CN)_2$. The free cyanide serves (*a*) to decrease the silver ion concentration, and thereby produce finer grained deposits, and in the use of "strikes" to prevent deposition of silver by immersion; (*b*) to increase the conductivity of the solution; (*c*) to increase the throwing power and (*d*) to aid in anode corrosion. According to Sanigar, with concentrations of free cyanide up to 200 per cent,

the silver deposits become softer, while with higher concentrations the deposits are harder.

In these solutions annealed rolled silver anodes of high purity (999 fine) should be employed. If the solutions contain an insufficient amount of free cyanide, there is a tendency for the anodes to become coated with silver cyanide or with silver peroxide (Ag_2O_2). The sodium or potassium carbonate serves to increase the conductivity but tends to retard anode corrosion unless considerable free cyanide is present. Alkali hydroxide and chloride also increase the conductivity, and are apparently not harmful. As the solutions are alkaline and the alkali cyanide and carbonate are both hydrolyzed (page 32) with the formation of hydroxyl ions, the conductivity is nearly proportional to the total concentration of solids, which in turn can be measured approximately by a hydrometer reading. The conductivity of most silver solutions is high, and under favorable conditions there is very little anode polarization or discharge of hydrogen at the cathode. Because of these facts and the relatively low current density generally employed, an e.m.f. of 1 to 2 volts is usually sufficient in silver plating. The cathode efficiency in silver deposition is usually very close to 100 per cent. The fact that silver is low in the electromotive series indicates that a very much higher potential is required to discharge hydrogen from silver solutions, even those containing much free cyanide, than to discharge hydrogen from corresponding copper cyanide solutions, in which latter, as noted on page 225, the cathode efficiency is low.[1]

4. SUGGESTED FORMULAS

In 1921 a valuable symposium[2] on silver plating was held in Sheffield, England. The conclusions of W. R. Barclay may be summarized as follows:

[1] *Cf.* Watts, O. P., and Braun, A., *Trans. Am. Electrochem. Soc.*, vol. 31, p. 303, 1917, and the discussion.

[2] Barclay, W. R., Electrosilver plating, *Trans. Far. Soc.*, vol. 16, p. 515, 1921.

Brook, G. B., and Holmes, L. W., The chemical composition of old silver plating solutions, *Trans. Far. Soc.*, vol. 16, p. 524, 1921.

Mason, F., A new maximum current density in commercial silver plating, *Trans. Far. Soc.*, vol. 16, p. 534, 1921.

Brook, G. B., The crystalline structure of electrodeposited silver, *Trans. Far. Soc.*, vol. 16, p. 538, 1921.

(*a*) The most suitable silver content is approximately 22 to 25 g./l. (3 troy oz./gal.).

(*b*) The proportion of free potassium cyanide should follow the molecular ratio (*i.e.*, be 100 per cent of the combined cyanide).

(*c*) The presence of such salts as the hydrate, carbonate, chloride, and cyanate (KCNO) is advantageous.

(*d*) The current density should be correlated with or proportional to the metal and free cyanide content of the solution. A current density of 0.3 to 0.33 amp./dm.^{2} (2.75 to 3 amp./sq. ft.) is recommended by Barclay.

(*e*) The temperature should be from 17 to 23°C. (63 to 73°F.).

(*f*) Cyanide should be added at regular intervals to maintain the specified free cyanide content.

(*g*) Baths give better results when used regularly than when used only intermittently.

Mason in his paper showed that with baths high in carbonate and cyanide a current density of 0.9 amp./dm.^{2} (8 amp./sq. ft.) can be used. Under favorable conditions current densities higher than those recommended by Mason have been employed by American platers.

F. C. Mesle[1] states that at 30°C. (86°F.), in baths containing brightener, an average current density of about 1.5 amp./dm.^{2} (15 amp./sq. ft.) can be used on moving cathodes, provided the maximum current density (*e.g.* on edges of spoons) does not exceed 3 amp./dm.^{2} (30 amp./sq. ft.). At lower temperatures the current density must be reduced. Higher temperatures decrease the throwing power. For a "dead white" deposit from solutions containing no brightener, an average current density of about 0.8 amp./dm.^{2} (8 amp./sq. ft.) may be used.

The following formulas are typical of those used in American practice:

(1)

First Strike for Steel	*N*	g./l.	
Metallic silver (Ag)	0.01	1.2	3 dwt./gal.
as Silver cyanide (AgCN)	0.01	1.5	0.2 troy oz./gal.
Copper carbonate ($Cu(OH)_2.CuCO_3$)	0.13	15	2 oz./gal.
Potassium cyanide (KCN)	1.0	68	9 oz./gal.

(2)

Second Strike for Steel, or First Strike for Brass, Nickel Silver, and Britannia			
Metallic silver (Ag)	0.05	5.0	12 dwt./gal.
as Silver cyanide (AgCN)	0.05	6.5	0.8 troy oz./gal.
Potassium cyanide (KCN)	1.0	68	9. oz./gal.

[1] *Monthly Rev. Am. Electroplaters' Soc.*, vol. 15, no. 10, p. 4, 1928.

(3)

Plating Solution for White Deposits	*N*	g./l.	
Metallic silver (Ag)	0.27	29	3.5 troy oz./gal.
as Silver cyanide (AgCN)	0.27	35	4.4 troy oz./gal.
Total potassium cyanide (KCN)	0.57	37	5.0 oz./gal.
Therefore free potassium cyanide (KCN)	0.30	19	2.5 oz./gal.
Potassium carbonate (K_2CO_3)	0.55	38	5.0 oz./gal.
or			
As silver chloride (AgCl)	0.27	39	4.7 troy oz./gal.
Total potassium cyanide (KCN)	0.84	55	7.3 oz./gal.
Therefore free potassium cyanide (KCN)	0.30	19	2.5 oz./gal.
Potassium carbonate (K_2CO_3)	0.55	38	5.0 oz./gal.

(4)

Plating Solution for Bright Deposits			
Metallic silver (Ag)	0.27	29	3.5 troy oz./gal.
as Silver cyanide (AgCN)	0.27	36	4.4 troy oz./gal.
Total potassium cyanide (KCN)	0.80	52	7.0 oz./gal.
Therefore free potassium cyanide (KCN)	0.53	34	4.5 oz./gal.
Potassium carbonate (K_2CO_3)	0.55	38	5.0 oz./gal.
or			
As silver chloride (AgCl)	0.27	39	4.7 troy oz./gal.
Total potassium cyanide (KCN)	1.07	70	9.3 oz./gal.
Therefore free potassium cyanide (KCN)	0.53	34	4.5 oz./gal.
Potassium carbonate (K_2CO_3)	0.55	38	5.0 oz./gal.

The mercury "blue dip" may be made by adding to a solution containing 7.5 g./l. (1 oz./gal.) of mercuric chloride ($HgCl_2$) about 4 g./l. (0.5 oz./gal.) of ammonium chloride (NH_4Cl). The mercuric cyanide solution may be prepared by dissolving 7.5 g./l. (1 oz./gal.) of yellow mercuric oxide (HgO) in a fairly strong solution, *e.g.*, 60 g./l. (8 oz./gal.) of sodium cyanide (NaCN).

Instead of adding carbon disulphide directly to the solution as a brightener, it is customary to add to a portion of the plating solution an excess of potassium cyanide and then to saturate it with carbon bisulphide, and to add small portions of this solution to the plating tank. This enables one to secure the desired very small concentration of carbon disulphide, and also insures that it can be quickly mixed with the plating solution. About 0.25 fl.oz. of carbon disulphide is shaken up with a gallon of solution containing 4 oz. of potassium cyanide, and the mixture is kept in a stoppered bottle. The carbon disulphide passes into

solution (or suspension) in the liquid. At regular intervals a definite quantity, *e.g.*, 4 fluid oz. of this solution is added to each 100 gal. of the solution in the tank. The stock solution contains about 2 c.c./l. or 0.25 fl. oz./gal. of carbon disulphide. The plating solution therefore contains only about 0.0007 c.c./l., or 0.0001 fl. oz./gal. of carbon disulphide, which is less than one part per million.

More frequent additions are required in warm than in cold weather, due no doubt to the greater evaporation of the carbon disulphide at the higher temperatures.

At various times efforts have been made to deposit alloys of cadmium and silver. This is readily possible because in cyanide solutions the potentials of these two metals lie close together. The process depends upon the addition of a suitable proportion of cadmium cyanide to a silver plating solution. The method has never been successfully applied, owing probably to the difficulty of maintaining a constant ratio of the two metals in the deposit. Recently it has been found that cadmium-silver alloys tarnish less readily than do those of pure silver.

5. ANALYSIS OF SOLUTIONS

The determinations most commonly made for control work are the free cyanide and the silver content. Carbonate can be estimated without much difficulty. Chloride, cyanate, and thiocyanate are difficult to determine in the presence of cyanide.

(a) **Free Cyanide.**—A 10-c.c. sample of the solution is diluted to 100 c.c. and is titrated directly with 0.1 *N* silver nitrate till a faint permanent turbidity is produced, which serves as the end point. As in this titration (page 48) each equivalent of silver nitrate reacts with two of sodium cyanide, 1 c.c. of 0.1 *N* $AgNO_3$ is equivalent to 0.0098 g. NaCN or 0.0130 g. KCN.

Example.—A 10 c.c. sample of the solution requires 22.2 c.c. of 0.1 *N* silver nitrate. The solution therefore contains

$$100 \times 22.2 \times 0.0130 = 28.9 \text{ g./l. free KCN}$$

or

$$100 \times 22.2 \times 0.0098 = 21.8 \text{ g./l. free NaCN}$$

or the solution is 0.44 *N* in free cyanide.

(b) **Silver.**—This may be determined *gravimetrically* as chloride. Ten cubic centimeters of the solution are treated in a well-

ventilated hood with an excess, *e.g.*, 5 c.c., of concentrated sulphuric acid, and the solution is boiled till the double cyanide is destroyed and the hydrocyanic acid is expelled. The residue is diluted with water to 150 c.c. and a slight excess of hydrochloric acid is added. The solution is well stirred, heated to boiling, and allowed to settle. The precipitate of silver chloride is filtered on a Gooch crucible, dried, and weighed. From the increase in weight the silver content can be calculated, using the factor $AgCl \rightarrow Ag = 0.753$.

Example.—If from 10 c.c. of the solution the AgCl = 0.288 g. the silver content = $100 \times 0.288 \times 0.753 = 21.7$ g./l. (2.6 tr. oz./gal.) of Ag.

Such a solution is 0.2 *N* in Ag. The cyanide required to form with it, the double cyanide, is $2 \times 0.2 = 0.4$ *N*. As the free cyanide as above determined was 0.44 *N*, the ratio of free to combined cyanide is 0.44 to 0.4, or 1.1 to 1.

The silver may be determined *volumetrically* provided it can be obtained in a solution free from cyanides. This can be accomplished by boiling with sulphuric acid as above, forming a solution which contains only silver sulphate and the alkali sulphates. Another simple way to prepare the solution is by precipitating the silver from 10 c.c. of the solution diluted to 100 c.c., by passing in hydrogen sulphide or by adding an excess of ammonium sulphide, $(NH_4)_2S$. The solution is heated for some time and the precipitated silver sulphide (Ag_2S) is filtered onto a filter paper, and washed with hot water. It is then dissolved by boiling with nitric acid, 1–1. The solution of silver sulphate or nitrate obtained by the above methods is titrated with standard sodium thiocyanate (sulphocyanate, NaCNS) solution, after the addition of a few drops of a solution (20 g./l.) of ferric alum, $(NH_4)_2SO_4.Fe_2(SO_4)_3.24H_2O$. The appearance of a faint pink color in the solution serves as the end point. The thiocyanate precipitates the silver as AgCNS, and when all the silver is thus combined the first drop of thiocyanate in excess combines with the ferric salt to form the red ferric thiocyanate. A 0.1 *N* sodium thiocyanate solution may be prepared by dissolving in water about 10 g./l. of the salt (NaCNS). As this is deliquescent, it is necessary to use more than the theoretical amount (8.1 g./l.) and to standardize the solution against the 0.1 *N* silver nitrate solution or against pure silver. This is done by dissolving a weighed amount of silver in nitric acid, expelling the oxides of nitrogen, diluting, and titrating as above.

Example.—If 0.423 g. of silver is dissolved and titrated, and requires 37.3 c.c. of the NaCNS solution, then

$$1 \text{ c.c.} = \frac{0.423}{37.3} = 0.0113 \text{ g. Ag}$$

Therefore the solution is $\frac{0.0113}{0.0108} = 0.105\ N$.

If now 10 c.c. of the plating solution treated as above require 24.2 c.c. of the NaCNS solution, the plating solution contains

$$100 \times 24.2 \times 0.0113 = 27.3 \text{ g./l. (3.3 troy oz./gal.) of Ag,}$$

or is 0.242 *N* in Ag.

The equivalent or combined cyanide would then be 0.48 *N*. If in this case the free cyanide is 0.44 *N*, the ratio of free to combined cyanide is 0.44 to 0.48, or 0.92 to 1.

(c) **Chloride.**—There is no simple accurate method for determining chloride in the presence of cyanide. Approximate results may be obtained by boiling 10 c.c. of the solution with 25 c.c. of (1-1) nitric acid till no further decomposition occurs. The solution is then diluted and the silver chloride is filtered out and dried on a Gooch crucible. The chlorine content is calculated as on page 38.

(d) **Carbonate.**[1]—This may be estimated by diluting a 5-c.c. sample of the solution to 100 c.c. with boiling water, and adding an excess, usually 10 to 15 c.c., of an approximately *N* barium nitrate $Ba(NO_3)_2$ solution (prepared by dissolving 130 g./l. of $Ba(NO_3)_2$ in recently boiled distilled water). The precipitate of barium carbonate ($BaCO_3$) is filtered out quickly and washed with hot water until the washings are neutral to litmus. The filter and precipitate are treated with an excess of *N* hydrochloric acid, thoroughly stirred and boiled, and after the $BaCO_3$ is completely dissolved, the excess of acid is titrated with standard alkali, using methyl orange as indicator.

Example.—If to the precipitate from 5 c.c. (1/200 l.) of the solution 20 c.c. of *N* HCl are added, and the titration with alkali requires 14.3 c.c. of *N* NaOH, then the $BaCO_3$ (or the K_2CO_3 originally present) is equivalent to $20 - 14.3 = 5.7$ c.c. *N* HCl. The potassium carbonate is therefore $\frac{5.7}{5} = 1.14\ N$, or the solution contains $1.14 \times 69 = 79$ g./l. (10.5 oz./gal.) of K_2CO_3.

(e) **Determining Weight of Silver Deposit.**—This may properly be considered as an analytical process connected with silver

[1] Brook, G. B., and Holmes, L. W., *Trans. Far. Soc.*, vol. 16, p. 527, 1921.

plating, as the weight of silver on plated goods is often specified. The silver may usually be determined by the loss in weight of the object when the coating is stripped off by an appropriate method, although for very accurate work it may be desirable to actually determine the silver in the resultant solution.

For *stripping* steel or britannia metal (either for analysis or for replating) it is most satisfactory to make the article the anode in a sodium or potassium cyanide solution, and to electrolyze till all the silver is dissolved off. Under proper conditions this operation does not attack the base metal and hence the change in weight after careful drying serves as a measure of the silver originally present. In this process the solution should be agitated, *e.g.*, by moving the articles to be stripped, in order to prevent the adherence of bubbles and consequent irregularity in the solution of the silver. It is not convenient to estimate the silver introduced into the solution from each piece, but if a number of similar articles are stripped, a sample of the solution may be analyzed for silver as above, and the average results thus checked. The silver may be recovered from the stripping solution either by precipitating silver chloride with hydrochloric acid (care!) or by electrolyzing with iron or carbon anodes. It may also be precipitated as metallic silver by means of powdered zinc (zinc dust).

Nickel silver and brass are best stripped by immersion in a heated mixture of 19 parts by volume of concentrated sulphuric acid and 1 part of concentrated nitric acid; or of 950 c.c. of concentrated sulphuric acid and 50 g. of sodium or potassium nitrate. Especially for stripping a considerable number of pieces to be replated, it is often advantageous to add a smaller amount of nitric acid at first, *e.g.*, only 10 c.c. to 950 of sulphuric acid, and then to add more as required to produce reasonably rapid action. By this method there is less chance of the base metal being attacked by the acid mixture.

In any case great care should be used to prevent entrance of moisture into the strip, which should be kept covered when not in use. It is placed in a duriron, stoneware or glass vessel, and very carefully heated on a sand bath or covered hot water bath until the temperature is about 80°C. (180°F.). The objects, which have been previously freed from grease, dried, and weighed, are suspended in the solution until all the silver has dissolved, which can be detected by the production of a dark

color over the entire surface. They are then rinsed, dried, and reweighed, and the loss in weight taken as the weight of silver. Here also the silver content of a portion of the solution may be determined occasionally as a check on the loss in weight of the objects.

Silver may also be stripped by the application of a reverse current with lead cathodes in concentrated sulphuric acid.

CHAPTER XX

GOLD AND PLATINUM PLATING

The metals gold and platinum are distinguished from the other metals in common use by the fact that they are not appreciably attacked by any single acid or by most reagents. Their use for ornamental purposes depends therefore not only upon their relative scarcity, high price, and pleasing appearance, but also upon the fact that they are not readily tarnished. Both gold and platinum are used for plating laboratory apparatus, such as calorimeter bombs, analytical weights, etc., where resistance to attack by fumes is desired.

It should be noted that these metals do not protect the base metal through any electrochemical action, as they are low in the electrochemical series, and therefore may actually accelerate the corrosion of the underlying iron, copper, or brass if the latter are exposed. The very high degree of protection furnished, for some time at least, by extremely thin gold coatings is an evidence that the coatings are very fine-grained and impervious. If produced from simple solutions such as the chloride bath, which is used in gold refining, the deposits are relatively coarse-grained. The fine structure produced in electroplating is therefore caused principally by the use of dilute solutions, and especially of the double cyanides (or ferrocyanides), in which the gold ion concentration is probably very low.

1. GOLD DEPOSITION

Gold solutions are usually prepared directly or indirectly from gold chloride ($AuCl_3$). This may be purchased in the form of crystals having the formula $AuCl_3.HCl.4H_2O$ (which may also be written as $HAuCl_4.4H_2O$, or chlorauric acid). These crystals contain, when pure, 48 per cent of gold. When, therefore, the weight of gold in a solution is specified, it is necessary to use almost exactly twice that weight of gold chloride crystals.

Gold chloride may be prepared by dissolving metallic gold in "aqua regia," a mixture of three volumes of concentrated hydro-

chloric and one of nitric acid. After the metal has all dissolved the solution is evaporated on a steam or water bath until crystals start to separate, and is then allowed to cool. Care must be used not be heat the residue much above 100°C. (212°F.), otherwise the auric chloride ($AuCl_3$) may be decomposed to form sparingly soluble aurous chloride (AuCl) or even metallic gold. In such a case the residue must be again treated with aqua regia and re-evaporated.

If gold chloride ($AuCl_3$) is treated with potassium cyanide, aurous cyanide (AuCN) and not auric cyanide $Au(CN)_3$ is precipitated, and on further addition of cyanide, this precipitate dissolves to form the double aurous cyanide, $KAu(CN)_2$:

$$AuCl_3 + 3KCN = AuCN + (CN)_2 + 3KCl$$
$$AuCN + KCN = KAu(CN)_2$$

The reduction and formation of the double aurous cyanide takes place on standing, or especially on boiling, and is accompanied by the evolution of cyanogen. (This reduction from auric to aurous in forming the double cyanide is analogous to the reduction from cupric to cuprous salts in forming the cyanide copper solution, p. 221.) It is possible under certain conditions to produce the double auric cyanide, but the gold in a cyanide plating solution is usually present in the aurous condition. This fact should be borne in mind in calculating the electrochemical equivalent of the gold.

According to the above reactions potassium chloride (KCl) is formed in the plating solutions prepared directly from the gold chloride. Its presence is usually not objectionable, though red spots are sometimes attributed to it. If the presence of potassium chloride is not desired, the gold may be first carefully precipitated by the addition of cyanide, and the precipitate of aurous cyanide filtered out and dissolved in potassium cyanide. It is also possible to purchase gold cyanide AuCN, which is now frequently used in making gold solutions. It contains when pure, 88 per cent of gold.

In some cases the solution of gold chloride is treated cautiously with ammonia (ammonium hydroxide, NH_4OH) until all the gold is precipitated as gold "fulminate." This is a complex compound containing gold, nitrogen, hydrogen, and oxygen, the exact formula of which is doubtful. When dried it is very explosive. It is therefore necessary to wash it by allowing it to

settle, and pouring off the clear solution. When gold fulminate is dissolved in potassium cyanide, the double aurocyanide is produced as above, and ammonia is liberated.

Gold solutions are also frequently prepared by the "porous cup" method. In this process an insoluble cathode, *e.g.*, of iron, is placed in the porous cup in a nearly saturated solution of potassium cyanide. The cathode should not touch the walls of the porous cup. Outside of the cup is placed a solution of potassium cyanide of the desired strength, *e.g.*, 22.5 g./l. (3 oz./gal.). An anode of pure gold, or of an alloy of a desired color, consisting of gold and silver for green gold or of gold and copper for red gold, is immersed in the outer solution. The current is then passed until the desired amount of gold or of the alloy is "run" into the solution, which may be determined by weighing the anode at intervals.

Three quite distinct methods for plating with gold are used in this country. These may be designated respectively as (*a*) gold electroplating, (*b*) salt water gold plating, and (*c*) dip gold plating. All three of these are in a certain sense electrolytic. Still another method, known as "fire-gilding," is used extensively, especially when thick coatings are desired. This latter method depends upon coating the brass articles with a gold amalgam (an alloy of gold and mercury), after which they are heated in a retort and the mercury is distilled off, leaving a relatively thick and very adherent layer of gold. Usually the articles are then given a very light plating with gold to produce the exact tint or "color" desired. The first three methods involve the following principles and solutions. In all methods the loss of gold by drag-out is very great unless special precautions are taken to recover it.

1. Gold Electroplating

This is a direct electrodeposition process, usually conducted with a solution of the double cyanide as above described, and with gold anodes. The solutions in use are all very similar in their constituents, but vary greatly in concentration. The extreme range in gold content is from 1 to 20 dwt./gal. (0.41 to 8.2 g./l). In general, the more concentrated solution is used when thick deposits are desired. To some extent, however, the metal content as well as that of other constituents is governed by the exact color or shade of gold desired. One of the condi-

tions that hinder the compilation of definite working formulas for gold plating is the great variety in the requirements of different plants or for different classes of work. In specific cases (page 366) silver, copper, or nickel are added to the gold solutions to secure desired colors or shades. A considerable range of colors may be obtained simply by adjusting the bath composition, temperature, and current conditions.

The gold solutions usually have a low content of "free cyanide." Sufficient is used to keep the anode bright and to secure enough anode corrosion to maintain the metal content. There is still considerable difference of opinion regarding the use of sodium or potassium cyanide, but the latter is more frequently used for gold plating. Small amounts of sodium phosphate increase the conductivity of the bath, and may, through complex formation, lower the metal ion content. In practice this salt is found to produce deposits of the lower karat shades. The following are typical formulas for the regular gold plating bath, although greater variations in concentration are often employed.

(1)	*N*	g./l.	
Metallic gold (as fulminate or cyanide)	0.01	2.1	5.0 dwt./gal.
Potassium cyanide	0.20	15.0	2.0 oz./gal.
Sodium phosphate ($Na_2HPO_4.12H_2O$)	0.03	4.0	0.5 oz./gal.
(2)			
Metallic gold (as fulminate or cyanide)	0.02	4.2	10.0 dwt./gal.
Potassium cyanide (KCN)	0.20	15.0	2.0 oz./gal.

These gold baths are usually run at a high temperature (60° to 80°C., or 140° to 176°F.) with pure rolled gold anodes and a low current density, *e.g.*, from 0.1 to 0.5 amp./dm.^{2} (1.0 to 5 amp./sq. ft.). The higher current density may be used in the more concentrated solutions or at higher temperatures. Even at these low current densities the rate of deposition is fairly high, owing to the large electrochemical equivalent of gold when in the aurous condition. If the metal content is maintained and the free cyanide is not too high, at the above temperatures and current densities the cathode efficiency is nearly 100 per cent. Hence ampere-hour meters (p. 187) can be used to advantage, especially for heavy deposits. In some cases platinum or hard gas-carbon anodes are used to replace about three fourths of the gold anodes. The justification for using insoluble anodes is that the gold content of the solution tends to increase if gold anodes are used. Platinum is, however, more expensive than

gold, so there is no economy (as there was in former years) in substituting platinum for gold anodes.

In many cases a light flash of gold is produced by plating for about 20 sec. in a solution such as (1) above, to "color" either (1) low karat gold articles, (2) articles previously gold plated and scratch brushed, or (3) base metal articles. In such cases the color may be governed either by the plating conditions or by the color of the underlying metal. The color is made more "pale" or yellow by either increasing the free cyanide content or by lowering the current density. A deposit over silver or nickel will have a lighter yellow color, and on copper a more reddish color than on brass. The composition of the brass also affects the color of gold deposited on it.

When very heavy gold deposits are required, a thin coating is applied from a cyanide bath, after which a gold chloride solution is used. Such a solution may contain about 16 to 32 g./l. (2 to 4 troy oz./gal.) of gold as chloride, with about 5 per cent of free hydrochloric acid. The solution may be prepared by dissolving the necessary amount of gold chloride in dilute hydrochloric acid; or by using gold anodes in a porous cup in dilute hydrochloric acid.

The production of "green gold," "red gold," and "white gold" depends upon alloy deposition and is subject to the general conditions for the simultaneous deposition of two metals (Chap. XXI). As, however, the operations are carried out so similarly to those of regular gold plating, they may for convenience be considered in this connection.

Gold deposits of 14 karat shades may be produced from solutions such as the following:

(3)			
Metallic gold (as fulminate or cyanide)	*N* 0.015	g./l. 3.1	7.5 dwt./gal.
Copper or nickel (as carbonate)	0.01	0.8	2.0 dwt./gal.
Potassium cyanide (KCN)	0.12	7.5	1.0 oz./gal.
Sodium phosphate (Na_3PO_4)	0.14	7.5	1.0 oz./gal.

Deposits produced at 50°C. (122°F.) at 0.2 amp./dm.^{2} (2 amp./sq. ft.) from such solutions contain only 1 to 2 per cent of copper or nickel, though they match in color rolled gold with 42 per cent of alloying elements.

Green gold is usually produced by the addition of sufficient double silver cyanide to a regular gold solution (containing 4 to 6

dwt./gal. of Au + Ag) to produce the desired tint. The solution is then run with platinum anodes, under which conditions the color remains nearly constant until most of the gold and silver is deposited; or green gold anodes, *i.e.*, alloys of gold and silver are used. The solution may also be prepared by the porous cup method, using as anodes an alloy of gold and silver with the desired color. A typical formula for a green gold solution is as follows:

(4)

	N	g./l.		
Metallic gold (as chloride)	0.01	2.1	5	dwt./gal.
Metallic silver (as chloride)	0.001	0.1	0.25	dwt./gal.
Sodium cyanide	0.6	30	4	oz./gal.

Small amounts of arsenious acid or of lead carbonate are often added to intensify the green color. These compounds are first dissolved in sodium hydroxide.

Red gold is prepared similarly by the addition of copper cyanide solution or of copper acetate to a gold bath.

White gold is secured by the addition of double nickel cyanide to a gold bath. A typical formula for a white gold solution is as follows:

(5)

	N	g./l.	
Gold (as fulminate) (Au)	0.01	2.1	5 dwt./gal.
Nickel (as cyanide) (Ni)	0.15	4.2	10 dwt./gal.
Ammonium chloride (NH_4Cl)	0.15	7.5	1 oz./gal.
Sodium cyanide (NaCN)	0.6	30	4 oz./gal.

Very little white gold plating is now done. Tin, nickel, and chromium are more commonly used to produce a white color on jewelry.

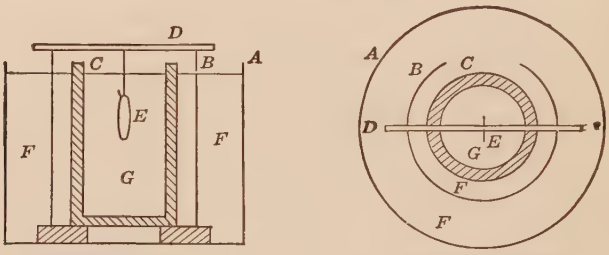
At present all these alloy gold baths are run on an empirical basis, as there has been no exhaustive study of the factors which determine the proportion of the metals deposited. The control of the operations is simplified by the fact that, just as in brass plating, the color and not the composition is usually specified.

2. Salt Water Gold Plating

When it is desired to apply a coating of gold which is very uniform in thickness and color and, which will withstand moderate service, but with less expense than with the regular gold plating,

the so-called "salt water process" is often used. In this process the gold solution is contained in a porous cup or pot, which is then placed in a copper vessel filled with a strong solution of sodium chloride (NaCl), in which a sheet of zinc is suspended. The arrangement is shown diagrammatically in Fig. 32.

This method involves the use of a primary cell or battery, in which the current is furnished by the zinc dissolving in the nearly saturated solution of sodium chloride. A little ammonium chloride is also sometimes added. The zinc, *B*, is therefore the anode of the cell, and the object *E* suspended from the rod *D* becomes the cathode, upon which the gold is deposited. In



Vertical Section Horizontal Section

FIG. 32.—Arrangement for Salt Water Gold Plating.

A—Copper Vessel
B—Sheet Zinc
C—Porous Pot
D—Cathode Rod
E—Object to be Plated
F—Sodium Chloride Solution
G—Gold Solution

principle, therefore, the process is an electrodeposition, in which the current is furnished by the cell instead of from an external source. This method is very similar to that used in the "Smee cell" for copper deposition before the development of the dynamo. The solution is usually heated to about 70°C. (158°F.), which also hastens deposition.

The gold solutions used in this process contain potassium ferrocyanide, $K_4Fe(CN)_6$, the so-called yellow prussiate of potash, or sodium ferrocyanide, $Na_4Fe(CN)_6$, and sodium phosphate and carbonate. It is difficult to assign a definite function to each of these constituents, especially the ferrocyanide. The gold may form a soluble double ferrocyanide, with low metal ion concentration. At least it is known that the deposits secured by this method are usually very dense, and hence a smaller weight of gold is required to meet such tests as the nitric acid dip, which is often specified for gold plating.

A typical formula for the gold solution in the salt water process is as follows:

(6)

	N	g./l.	
Gold (as fulminate)	0.006	1.2	3.0 dwt./gal.
Sodium ferrocyanide, $Na_4Fe(CN)_6.10H_2O$	0.12	15.	2.0 oz./gal.
Sodium phosphate ($Na_2HPO_4.12H_2O$)	0.06	7.5	1.0 oz./gal.
Sodium carbonate (Na_2CO_3)	0.08	4.	0.5 oz./gal.
Sodium sulphite (Na_2SO_3)	0.002	0.15	0.2 oz./gal.

Very often, however, solutions with only 1 dwt./gal. of gold are used in this process. The solution is usually boiled for about 30 min. and filtered before use.

3. Dip Gold Plating

The dip gold process is used especially for plating cheap small objects, upon which only a very thin coating of gold is justified. It is surprising how little gold is required to produce a relatively impervious coating. It is known that on small brass metal novelties, a coating with as little as 8 to 20 cts. worth (2 to 5 grains) of gold per gross will under favorable conditions withstand a brief immersion in nitric acid. If we assume as a rough approximation that the average area on each of such articles is about 2 cm.^{2} (0.3 sq. in.) the average thickness of the deposit with 2 grains of gold per gross is only about 0.0002 mm., or 0.000008 in. Actually the deposits are often much thinner, *e.g.*, 0.000025 mm. (0.000001 in.).

In the dip process the gold is deposited by immersion, *i.e.*, by the replacement of the gold of the solution by the zinc or copper of the brass base metal. It is rather surprising that such dense deposits are produced. This may be partly due to the high electrochemical equivalent of the gold in the aurous condition. If for simplicity we assume that the gold is replaced by the zinc of the brass, the weight of gold deposited is about six times that of the zinc dissolved. As, however, the specific gravity of the gold is nearly three times that of zinc, the *volume* of the gold deposited is about twice that of the zinc dissolved. Under these conditions it is obvious that there will be a tendency for the gold to form a very dense deposit.

Although under usual conditions almost any metal will deposit gold by immersion, good deposits are obtained only upon copper or brass. It is therefore customary to plate copper or brass

or so-called "bronze" upon articles of steel, nickel silver, die castings, or other metals which are to be subsequently gold plated, especially by the dip process.

The solutions used for dip gold are usually similar to, but more complicated than, those for the salt water process. Formerly in addition to the gold compound, ferrocyanide, phosphate and carbonate, ferric chloride, the so-called "sesquichloride" ($FeCl_3.6H_2O$) was often added, and sometimes sodium hydroxide (NaOH). It is impossible even to suggest the function of each constituent in so complicated a bath as this. In recent years solutions containing cyanide instead of ferrocyanide have been used for the dip gold process. A typical modern formula for this solution is as follows:

(7)

	N	g./l.	
Gold (as fulminate).....	0.01	2.1	5 dwt./gal.
Sodium carbonate (Na_2CO_3).	0.90	45.0	6 oz./gal.
Sodium cyanide (NaCN)...	0.60	30.0	4 oz./gal.

The dip gold solutions are boiled for a few hours in a stone crock or in an enameled iron kettle before use, and are operated at a temperature of about 80°C. (176°F.).

4. Analysis of Solutions

The principal determinations made upon the gold plating solutions are of the metal and the free cyanide. The latter may be determined by direct titration with silver nitrate in the usual way (page 230).

The gold content of the solutions is frequently determined by a fire assay. In this process a definite volume, *e.g.*, 100 c.c. of the gold solution, is evaporated to a small volume and mixed with litharge (PbO). The mass is dried and heated to fusion in a fireclay crucible, whereby a "button" of lead is produced, which contains all of the gold and silver that were present in the solution. This lead button is heated in a muffle furnace upon a "cupel" of bone ash, and the lead is oxidized, leaving a small bead containing the gold and silver. This is weighed, and if silver is present (as, *e.g.*, in green gold solutions), the metals are parted by treatment with nitric acid.

A much simpler method is to destroy the cyanide by evaporating in a hood a portion, *e.g.*, 50 c.c., of the solution with an

excess of hydrochloric acid. To the resulting solution is added an excess, *e.g.*, 50 c.c., of a filtered 0.5 *N* solution (70 g./l.) of ferrous sulphate ($FeSO_4.7H_2O$). The solution is allowed to stand several hours, after which the metallic gold, which is precipitated as a fine powder, is filtered out and ignited and weighed.

Hydrogen peroxide may also be used to precipitate the gold. In this case 10 c.c. of the solution is evaporated to dryness with 3 c.c. of conc. HNO_3, and the residue dissolved in aqua regia, of which the excess is expelled by evaporation. The solution is diluted and neutralized with sodium hydroxide. An excess of hydrogen peroxide is then added to precipitate the gold.

The gold may also be determined in the solution after the evaporation with hydrochloric acid, by the addition of potassium iodide in excess, and the titration of the liberated iodine with sodium thiosulphate. In this operation the gold is first reduced from the auric to aurous condition:

$$AuCl_3 + 3KI = AuI + I_2 + 3KCl$$

In practice it is necessary to add an excess of potassium iodide solution, and a few drops of starch solution, which produces a blue color. A 0.01 *N* $Na_2S_2O_3$ solution is then run in until the blue color disappears, and a slight excess of thiosulphate is added. This excess is titrated with 0.01 *N* iodine solution. The value of the thiosulphate solution is determined by titrating a known amount of gold under similar conditions. The ratio between the thiosulphate and iodine solutions must be determined frequently by direct comparison, using starch as indicator.

Example.—0.04 g. of gold was dissolved in aqua regia, evaporated to dryness on a water bath, and treated as above, and required 47.2 c.c. of $Na_2S_2O_3$ solution, and 5.2 c.c. of I_2 solution. These two solutions were found to have a ratio such that 10 c.c. of I_2 solution required 11.2 c.c. of $Na_2S_2O_3$. Therefore the 5.2 c.c. I_2 are equivalent to $\frac{11.2}{10} \times 5.2 = 5.8$ c.c. of $Na_2S_2O_3$; and the gold required $47.3 - 5.8 = 41.4$ c.c. of $Na_2S_2O_3$. 1 c.c. of $Na_2S_2O_3$ therefore equals $\frac{0.04}{41.4} = 0.00097$ g. Au.

25 c.c. of the gold plating solution required 42.6 c.c. of $Na_2S_2O_3$ and 3.2 c.c. of I_2. Then $3.2 \times \frac{11.2}{10} = 3.6$ c.c. of $Na_2S_2O_3$ excess were used, or the gold required $42.6 - 3.6 = 39$ c.c. of $Na_2S_2O_3$. The solution therefore contains $40 \times 39 \times 0.00097 = 1.51$ g./l. $= \frac{1.51}{0.41} = 3.7$ dwt./gal.

If nickel is present in a gold solution, it may be determined in the filtrate obtained by precipitating the gold with ammonium hydroxide from a sample of the plating solution which has been evaporated with acid and taken up in aqua regia. The nickel is precipitated by dimethylglyoxime, and the precipitate filtered onto a Gooch crucible, dried at 120°C., and weighed. The precipitate contains 20.3% Ni.

2. PLATINUM PLATING

In former years when platinum was less expensive, the so-called "French gray" or other "oxidized" finishes on silverware were often produced by immersing the silver plated articles in a warm, weak aqueous or alcoholic solution of platinic chloride ($PtCl_4$) or, more strictly speaking, chlorplatinic acid (H_2PtCl_6), such as is secured by dissolving platinum in aqua regia. The platinum was deposited in the form of a black or gray powder. The scarcity and increased cost of platinum has led to the discontinuance of this method.

Electroplating with platinum has only a limited application. For many purposes where platinum deposits might be desired or expected, nickel, chromium or tin is applied.

1. Suggested Formulas

Many solutions have been proposed for plating with platinum, but the only one which has been extensively applied in this country is the mixed phosphate solution, of the type long since recommended by Roseleur. The following is essentially the formula recommended by him.

(1)

	N	g./l.	
Platinum (as chloride)	0.1	5	12 dwt./gal.
Ammonium phosphate, $(NH_4)_2HPO_4$	1.0	45	6 oz./gal.
Sodium phosphate ($Na_2HPO_4.12H_2O$)	2.0	240	32 oz./gal.

In preparing this solution, the three compounds are dissolved separately in water and the ammonium phosphate solution is added to the platinic chloride. This produces a yellow precipitate of ammonium chlorplatinate, $(NH_4)_2PtCl_6$. Without filtering this solution the sodium phosphate solution is added, which dissolves the yellow precipitate. The mixture is then boiled for a few hours, or at least until no odor of ammonia can be

detected, and the solution has a pale lemon yellow color. It is not possible to state just what is the final product in the solution. It appears probable that the platinum is still present in the platinic form (Pt^{IV}), probably as a double or mixed phosphate, or as an "ammino" compound. As the platinic chloride usually contains some free hydrochloric acid (combined to form H_2PtCl_6), and as some ammonia is evolved during the boiling, it appears probable that the final solution contains an appreciable amount of the primary phosphates such as NaH_2PO_4 and $NH_4H_2PO_4$.

A modification of the phosphate bath is as follows:

(2)

	N	g./l.	
Platinum (as chloride)	0.08	4	10 dwt./gal.
Ammonium phosphate, $(NH_4)_2HPO_4$	1.00	45	6 oz./gal.
Boric acid (H_3BO_3)	0.50	15	2 oz./gal.

Platinum solutions are operated at a temperature of about 70°C. (158°F.), and with a low current density, usually less than 0.1 amp./dm.^{2} (1 amp./sq. ft.). Difficulty is experienced in securing thick impervious deposits of platinum from this or other solutions. The thin deposits are found to exert very little protection against the action of acids or fumes, owing to the fact that they usually have fine cracks, probably caused by contraction of the platinum during deposition. Their structure is much like that of chromium deposits, (p. 126).

A very special application of platinum deposition is the coating of electrodes with platinum black for use in conductivity and hydrogen ion concentration measurements. In this process a solution of chlorplatinic acid containing about 30 g./l. of metallic platinum is used. Two electrodes to be plated are usually made the anode and cathode, and the current is reversed about every 3 min. A current density just sufficient to produce hydrogen evolution is used. The addition of a small amount of lead acetate is a common practice. In some way it fosters the production of the black spongy deposit that is desired.

2. Analysis of Solution

The platinum in the solution can be determined by precipitating it with granulated metallic zinc, the excess of which is dissolved with dilute hydrochloric acid. The precipitated platinum can then be filtered out, ignited, and weighed.

Ammonia can be determined by the usual method, *i.e.*, distillation with an excess of alkali into standard acid (page 263).

The phosphate can be determined in the solution from which the platinum has been removed by means of zinc. To this solution a few grams of ammonium chloride are added and then an excess of "magnesia mixture" (a solution of magnesium chloride, ammonium chloride, and ammonia). An excess of ammonium hydroxide is added, and on standing a precipitate of magnesium ammonium phosphate ($MgNH_4PO_4$) is formed, which is filtered out, ignited, and weighed as magnesium pyrophosphate ($Mg_2P_2O_7$), from which the phosphate content can be calculated.

CHAPTER XXI

DEPOSITION OF ALLOYS

1. GENERAL PRINCIPLES

Although it is well known that under certain conditions it is possible to deposit two metals simultaneously from a solution containing both, the only alloy which is deposited successfully on a commercial scale is brass.[1] Brass plating of iron has been very extensively applied during recent years. Brass deposits are usually quite thin and exert little protection against corrosion. Their function is therefore chiefly ornamental, and brass plating may in many cases be considered as simply a means of coating iron or steel to imitate brass. For indoor use, where it is not exposed to corroding influences, brass plated hardware may serve a very useful purpose. The fact that it is used to replace solid brass is not in itself an indictment against its use, any more than the application of silver plated tableware is subject to criticism. The chief criticisms of brass plating arise from occasions when it has been employed for entirely inappropriate purposes, such as upon outdoor hardware and fittings, or where it has been fraudulently substituted for solid brass.

Although certain general principles of alloy deposition are fairly well established, their application involves a knowledge of so many at present undefined variables that very little immediately useful information has thus far been secured by research. In consequence, we find that brass plating has been developed and is being conducted almost entirely upon an empirical basis. Even in those few plants where the composition of the baths, anodes, and deposits is carefully controlled by chemical analysis, the conditions employed have usually been selected arbitrarily as those which for a given class of work yield deposits of the desired color or appearance. The inability of science to predict

[1] The deposition of a true bronze, *i.e.*, a copper-tin alloy, has never been extensively applied on a commercial scale. In most cases the so-called "bronze plating" is conducted in brass plating solutions with high copper content.

the best conditions of operation for these and many other plating operations should not be considered as a ground for criticism of science, but rather as an argument for more extended researches in this field, coordinated in every possible way with practical knowledge and experience.

The fundamental principle which governs the simultaneous separation of two metals from a solution is the same as that which determines the cathode efficiency of deposition of any single metal. It has been pointed out that in most cases when the metal cathode efficiency is less than 100 per cent, hydrogen is evolved in amount corresponding to the deficiency, or, in other words, the cathode efficiency of the metal plus hydrogen (plus any other changes in valence) is always 100 per cent. We may therefore consider that when a metal and hydrogen are discharged at the cathode, we have in a certain sense the deposition of an alloy.

Throughout this text emphasis has been laid upon the potentials and positions of the metals in the electrochemical series. It has been explained that those metals which are below hydrogen, such as copper and silver, may be readily deposited from acid solutions, *i.e.*, those with a high concentration of hydrogen ions, with high cathode efficiency, or without appreciable hydrogen evolution. On the other hand, those metals, such as nickel, iron and zinc, which are above hydrogen, cannot be deposited with high efficiency from strongly acid solutions at moderate current densities. In an acidified copper sulphate solution normal in copper ions and in hydrogen ions, the single potential of copper is + 0.34 volt higher than that of hydrogen. Therefore from such a solution the deposition of hydrogen will require a cathode potential 0.34 volt greater than is necessary to deposit copper. Hence the cathode efficiency from such a solution is very high and little or no hydrogen is evolved under normal conditions. If, however, the concentration of copper ions is decreased, *e.g.*, by dilution (as may occur at the cathode in still solutions), or if the concentration of hydrogen ions is increased, *e.g.*, by the addition of acid, the potential of copper decreases and that of hydrogen increases, and the two approach each other. When these two potentials are equal it is as easy to discharge hydrogen as to discharge copper, hence the two will be liberated simultaneously in the proportion in which the two ions are present in the solution adjacent to the cathode. If the two potentials are nearly but not exactly equal, both

elements may be liberated, in proportions dependent upon both their respective potentials and ion concentrations.

If we apply the same principle to two metals, it is equally true that for the two to be deposited their cathode potentials in the solution involved must be nearly if not exactly equal. Consideration of the electrochemical series shows that the *normal* potentials of two metals are seldom very close. Those of lead and tin are quite close to each other, and actually these two metals can be readily deposited from acid fluoborate solutions in the form of an alloy. The normal potentials of copper and zinc lie very far apart, however (+0.34 and −0.76 volt respectively), so that it is not practicable to deposit these two metals simultaneously from solutions of their simple salts, such as the sulphates, in which the metal ion concentrations are relatively high.

It has been pointed out that the cyanide solutions of copper and zinc contain very small concentrations of their respective ions. If by the formation of complex cyanides the metal ion concentrations of copper and zinc were reduced proportionally, we would still have a great difference in their corresponding single potentials. Brass plating is rendered possible by the fact that in forming double cyanides, especially with an excess of cyanide, the potential of copper is reduced more rapidly than that of zinc, and finally the two potentials become equal. By still further addition of the cyanide, the potential of copper may be made lower than that of zinc; in other words, a solution can be produced in which copper can precipitate zinc by immersion.

2. LEAD-TIN ALLOYS

The simple principles of alloy deposition can be illustrated by consideration of lead-tin alloys, produced from fluoborate solutions.[1] This operation has been carried out successfully by the U. S. Navy Department in recent years, and for certain purposes such deposits may have a definite though limited commercial application. The process is of considerable interest because it is much simpler in certain respects than is brass plating and therefore lends itself more readily to investigation. The cathode efficiency over a wide range of conditions is nearly 100 per cent and the solutions do not change in composition as readily

[1] Blum, W., and Haring, H. E., *Trans. Am. Electrochem. Soc.*, vol. 40, p. 147, 1921.

as do brass solutions. The following conclusions were drawn from the above study:

(*a*) Lead and tin have nearly equal potentials in fluoborate solutions, but under similar conditions the tin appears to have the lower potential, *i.e.*, the greater solution pressure.

(*b*) Lead or tin may each displace the other from fluoborate solutions, depending upon their respective metal ion concentrations.

(*c*) Solutions which are 1.0 *N* in metal and 0.5 *N* in free HBF_4, when agitated with tin or lead reach equilibrium at about 0.81 *N* Sn and 0.19 *N* Pb, because then the two metals have the same potential. This equilibrium is not affected by glue but is influenced appreciably by the acidity and total metal concentration.

(*d*) The cathode efficiencies under normal conditions are so nearly 100 per cent that the composition of the deposits can be calculated from the weight of metal deposited by a given quantity of electricity. The latter may be measured with a lead or copper coulometer.

(*e*) The composition of the deposits obtained under otherwise similar conditions depends upon the metal ratio in the solution. The ratio of the metals in the deposit is the same as that in the solution only when the solution has the equilibrium composition as above defined.

(*f*) Increasing the current density, in solutions of low tin content, increases the tin content of the deposit.

(*g*) The presence of glue has the same effect upon the metal ratio in the deposit as has an increase in current density.

(*h*) The composition of the deposit is not influenced by that of the anodes, except as these cause changes in the solution.

(*i*) Continuous operation with anodes containing more or less tin than corresponds to the equilibrium solution (81 equivalent per cent or 71 weight per cent of tin) causes the formation of deposits differing from the anodes always in the direction of this equilibrium. Thus if the anodes contain less than 71 weight per cent of tin, the deposits will contain more tin than the anodes, and vice versa.

(*j*) To produce deposits containing about 50 weight per cent of tin, the solution may be prepared by electrolyzing a lead fluoborate solution (page 339) with tin anodes until, as determined by calculation or analysis, the deposit contains nearly the desired

tin content. During this operation the solution should be agitated or at least frequently mixed. Lead-tin anodes are then used which contain somewhat less tin than is desired in the deposits. A current density of 0.5 to 1.5 amp./sq.dm. (4.7 to 14 amp./sq. ft.) may be employed.

(*k*) Deposits of lead and tin have a finer crystalline structure than lead or tin deposited under similar conditions.

(*l*) In the presence of glue the deposits are still finer grained.

3. BRASS PLATING

(a) **Principles.**—Some of the above conclusions apply to brass plating. The fundamental problem of brass plating is to find that composition of solution in which the potentials of the two metals are equal, or, more strictly speaking, in which these potentials and the metal ion concentrations are such that an alloy of the desired composition or color will be deposited. This is not, however, a simple problem because in these cyanide solutions there is a considerable cathode polarization and hence a higher potential than the equilibrium potential must be applied in order to produce any specific current density. It is therefore necessary to study for these metals in each solution not only the equilibrium potentials but also the cathode potential—current density curves (p. 71). Even when the relative current densities of deposition of the two metals are determined it is necessary to learn their relative cathode efficiencies under those conditions. It is well known that in brass plating there is sometimes considerable evolution of hydrogen, in other words, we are dealing with the simultaneous deposition not of two but of three elements. Moreover, it is known that the presence of each metal may change the discharge potential of the other by the formation of alloys, generally "solid solutions," which have a potential intermediate between the two metals. Although it is not possible to deposit metallic sodium from an aqueous solution on most metal cathodes, it is possible to do so upon a mercury cathode, for the reason that an alloy or amalgam is formed having a lower solution pressure than the sodium. Similarly, it has been shown that the potential of electrodeposited brass is intermediate between that of zinc and copper, which is evidence that there is at least some tendency to form an actual alloy at the cathode. X-ray examinations have also shown that the deposited brass is an alloy, and not simply a mixture of copper and zinc.

The above considerations have been discussed, not so much with a view to explaining or predicting the favorable conditions for brass deposition, but rather to emphasize the very extended researches that must be conducted before such predictions can be safely made. Such research must involve the study of solutions containing not only the two double cyanides and free cyanide, but also those containing other compounds, such as ammonia, carbonate, free alkali, sulphate, sulphite, arsenic, and other substances which may be formed in or introduced into the solutions. Much valuable work has been conducted upon this subject,[1] but it is difficult to deduce from these investigations the best operating conditions.

From a practical standpoint the control of brass plating involves the maintenance of a composition of solution which at the temperature and current density employed will produce the desired deposit. Fortunately it is the color and not the actual composition of the deposit that is important, and after considerable experience the plater can, as required, change one or another condition in order to secure or match a certain color of brass. In order to operate satisfactorily it is necessary that the copper and zinc should dissolve from the anodes in approximately the same proportion in which they are deposited, otherwise the solution must be frequently replenished by appropriate additions. The metals are best supplied by the use of brass anodes of the desired composition. Separate copper and zinc anodes have at times been used commercially, but considerable difficulty is experienced in causing them to dissolve in the proper ratio. It is not essential, though it is usual, for the solution to contain the two metals in about the same proportion as they are in the anodes and in the deposit. That the composition of the solution may remain constant in spite of the fact that the deposit has a different metal ratio than the solution is evident from the following. Suppose that it is desired to produce a deposit containing 75 per cent copper and 25 per cent zinc, and that it has been found empirically that such a deposit can be produced from a solution containing 3 oz./gal. of copper and 2 oz./gal. of zinc,

[1] Ferguson, A. L., and Sturdevant, E. G., *Trans. Am. Electrochem. Soc.*, vol. 38, p. 167, 1920. (This paper also includes a bibliography of the subject.) And Bennett, C. W., *Trans. Am. Electrochem. Soc.*, vol. 23, p. 231, 1913; and Bennett, C. W., and Davison, A. W., *Trans. Am. Electrochem. Soc.*, vol. 25, p. 347, 1914.

i.e., with the two metals in the ratio of 60 to 40 per cent. One hundred gallons of such a solution would then contain 300 oz. of copper and 200 oz. of zinc. If, now, it was operated with anodes containing 75 per cent copper and 25 per cent zinc, and 40 oz. of metal (*i.e.*, 30 oz. of copper and 10 oz. of zinc) was dissolved from the anodes and the same quantities were deposited on the cathodes, the solution would still contain 300 oz. of copper and 100 oz. of zinc.

The actual proportion of metals required in the deposits to secure a desired color may be appreciably different from that in cast or rolled brass of the same color. Thus it has been found that to imitate a common high brass containing 65 per cent copper and 35 per cent zinc, the deposit must contain about 80 per cent of copper. Therefore anodes of this composition are usually employed. For a greener brass deposit, a solution containing the copper and zinc in the ratio of 75:25 is preferable.

The proper ratio of copper to zinc in the solution to produce deposits of the above composition and color depends upon the free cyanide content, the total metal content, the temperature, and the current density employed. It is possible to secure such deposits from solutions containing the copper and zinc in the ratio of 4 to 1, although in some cases the relative copper content of the solution is lower than that of the anode or cathode, *e.g.*, 3 to 1 if the deposit is to be in the ratio of 4 to 1. It is very difficult to predict the exact effect of changes of the above conditions. Within certain limits an increase in free cyanide decreases the proportion of copper in the deposit, because thereby the potential of the copper approaches or may pass that of zinc. Unless considerable free cyanide is present, it is easier to deposit copper than zinc, hence the normal deposit contains a higher proportion of copper than does the solution. Increasing the current density decreases the copper content of the deposit. This may be readily confirmed by noting that on inaccessible parts such as the back of the cathode, where the current density is low, the deposit is reddish and high in copper. Elevating the temperature of the solution increases the copper content of the deposit.

In a recent study of brass plating,[1] it was found that brass deposits with an 80:20 composition can be produced from a solution containing the copper and zinc also in the ratio of 80:20,

[1] Reported by G. B. Hogaboom and W. V. Coleman to the American Electroplaters' Society in July, 1929.

with a total metal content of at least 22.5 g./l. (3 oz./gal.). The free cyanide content should be about one-fourth of the total combined cyanide. About 30 to 60 g./l. (4 to 8 oz./gal.) of sodium carbonate is beneficial, and small additions of ammonia should be made occasionally. At a temperature of about 40°C. (104°F.) flexible brass deposits of the above composition can be produced at a current density of about 0.3 amp./dm.^{2} (2.8 amp./sq. ft.).

The above authors also found that rolled brass anodes containing 80 per cent copper and 20 per cent zinc dissolve satisfactorily. Rolled anodes that have been annealed at about 500°C. (930°F.) corrode more uniformly than unannealed anodes.

In calculating the anode and cathode efficiencies in brass plating, it may most conveniently be assumed that the current which actually dissolves or deposits metal is divided between the two metals in the proportion in which they are present in the anode or cathode. This is equivalent to assuming that the efficiencies are equal with respect to each metal. Suppose for example that in a certain case a current of 1.5 amp. was passed for 1 hr. (*i.e.*, 1.5 amp.-hr. as measured with a copper coulometer) and that 2.60 g. of metal actually dissolved from an anode containing 82 per cent copper and 18 per cent zinc; and that 2.70 g. of metal deposited on the cathode and contained 80 per cent copper and 20 per cent zinc. Then on the above assumption the anode and cathode efficiencies can be calculated as follows.

From Table 9 in the appendix it may be seen that from cuprous salts (with a valence of 1) such as are present in brass solutions, 1 amp.-hr. will dissolve or deposit (at 100 per cent efficiency) 2.37 g. copper. From zinc solutions 1 amp.-hr. will dissolve or deposit 1.22 g. of zinc.

To dissolve 100 g. of an 82:18 brass anode, *i.e.* 82 g. of copper and 18 g. of zinc, will require $82/2.37 = 34.6$ amp.-hr. for the copper and $18/1.22 = 14.8$ amp.-hr. for the zinc or a total of 49.4 Therefore the equivalent weight of an 82:18 brass will be $100/49.4 = 2.02$ g./amp.-hr. and 1.5 amp.-hr. will dissolve (at 100 per cent efficiency) $1.5 \times 2.02 = 3.03$ g. If however only 2.60 g. dissolves, the anode efficiency is $2.60/3.03 = 86$ per cent.

Similarly to deposit 100 g. of brass containing 80 per cent copper and 20 per cent zinc, will require

$$\frac{80}{2.37} = 33.8 \text{ amp.-hr.}$$

plus

$$\frac{20}{12.2} = 16.4 \text{ amp.-hr.}$$

A total of 50.2 amp.-hr.

Hence 1 amp.-hr. is equivalent to 100/50.2 = 1.96 g. brass (80:20) and 1.5 amp.-hr. will deposit, at 100 per cent efficiency, 1.5 × 1.96 = 2.94 g. If only 2.70 g. is deposited the cathode efficiency is 2.70/2.94 = 92 per cent.

Such data would indicate simply that under the conditions employed, the metal *content* of the solution was kept approximately constant, but not necessarily the metal ratio in the solution. The latter must be determined from time to time and corrected if necessary. Actually, as indicated in this example, it is usually desirable to employ anodes with a slightly higher copper content than in the deposits, as then there is less formation of sludge on the anodes, and the copper content of the solution is maintained. At intervals zinc cyanide may then be added to the solutions in the amounts indicated by analyses.

Recent observations have shown that the control of the pH of brass plating solutions is feasible and advantageous. The optimum pH is about 11, as determined colorimetrically. The indicator is prepared by dissolving 0.1 g. of phenolphthalein and 0.6 g. of thymolphthalein in 300 c.c. of 50 per cent ethyl alcohol. This mixed indicator has a range from 8.3 to 11. The pH measurement should be made after the content of metal and cyanide has been adjusted to the desired value. If then, as commonly occurs, the pH is found to be too low, because the solution tends to become less alkaline, sodium hydroxide, NaOH, or ammonium hydroxide, NH_4OH, is added to produce the desired pH. If the pH is too high, dilute sulphuric acid, H_2SO_4, is very *carefully* added to produce the desired pH.

In brass plating certain addition agents are often used as "brighteners." Formerly the most common of these was arsenic, added in the form of arsenic trioxide (As_2O_3) or of sodium arsenite (Na_3AsO_3). In either case the latter compound is formed in the alkaline solution. It is not known whether from such solutions any arsenic is deposited with the brass, or to what property the brightening effect may be due. It is possible that very small amounts of arsenic in the deposit may aid in depolarizing the deposition of zinc at the cathode, and thereby foster the pro-

motion of an alloy relatively high in zinc content. Solutions containing arsenic are, however, very difficult to operate. For several years carbolic acid (phenol, C_6H_5OH) has been successfully used as an addition agent in brass solutions. Relatively high concentrations, *e.g.* 0.3 to 0.45 g./l. (0.04 to 0.06 oz./gal.) may be employed.

(b) **Suggested Formulas.**—So many formulas have been suggested for brass plating and so few of the commercial brass solutions are controlled by analysis, that it is difficult to specify exact formulas or even the limits of concentration. The total metal content is usually from 15 to 30 g./l. (2 to 4 oz./gal.). The ratio of copper to zinc in the solutions varies between the extremes of 2 to 1 and 4 to 1, the copper therefore corresponding respectively to 67 and 80 per cent of the total metal content. In calculating the relative normalities it is necessary to take into account the fact that the copper is in the cuprous (Cu^{+I}) state while the zinc has a valence of two (Zn^{+II}). Normal solutions will therefore contain respectively 64 g./l. of copper and 33 g./l. of zinc or nearly in the ratio of 2 to 1. If, then, in a solution which was 0.5 *N* in each metal, the potentials of the copper and zinc were exactly equal, the deposit would contain not equal but equivalent amounts of these metals, *i.e.*, the actual percentages, would be in the proportion of approximately 2 to 1, which approaches roughly the ratio desired in brass plating.

The simplest method of preparing the solutions is by dissolving copper and zinc cyanides in sodium cyanide, of which an excess is always present. Suppose that it is desired to prepare a solution to contain a total of 22.5 g./l. (3 oz./gal.) of metal, with the copper and zinc in the ratio of 4 to 1. The solution would require 18 g./l. (2.4 oz./gal.) of copper and 4.5 g./l. (0.6 oz./gal.) of zinc. These quantities are equivalent to $18/64 = 0.28$ *N* copper, and $4.5/33 = 0.14$ *N* zinc. If prepared from the metal cyanides it will require $0.28 \times 90 = 25.2$ g./l. of CuCN; and $0.14 \times \frac{118}{2} = 8.3$ g./l. of $Zn(CN)_2$. To dissolve them will require an amount of sodium cyanide equivalent to the zinc cyanide plus twice the copper cyanide (forming 2NaCN.CuCN and $2NaCN.Zn(CN)_2$). Therefore it will need $2 \times 0.28 + 0.14 = 0.70$ *N* NaCN, or $0.70 \times 49 = 34$ g./l. of NaCN. The total combined cyanide is then $0.28 + 0.14 + 0.70 = 1.12$ *N*. If it is desired to have the free cyanide equal to 30 per cent of the

combined cyanide, the solution will require an addition of $0.3 \times 1.12 = 0.34$ *N* NaCN. $0.34 \times 49 = 16.7$ g./l. (2.2 oz./gal.) of free NaCN. When such a solution is prepared from the metal cyanides it is customary to add sodium carbonate, *e.g.*, 30 g./l. or 4 oz./gal. of Na_2CO_3. The actual formula of the above solution may be rounded off as follows in terms of commercial chemicals:

(1)*a*	*N*	g./l.	oz./gal.
Copper cyanide (CuCN)	0.30	27	3.6
Zinc cyanide, $Zn(CN)_2$	0.15	9	1.2
Sodium cyanide (NaCN)	1.10	54	7.5
Sodium carbonate (Na_2CO_3)	0.60	30	4.0
Copper content (Cu)	0.30	19	2.5
Zinc content (Zn)	0.15	5	0.65
Free sodium cyanide (NaCN)	0.35	17	2.3

A practically identical solution can be made by dissolving basic copper carbonate and zinc carbonate in sodium cyanide. To prepare the above solution from these constituents will require the following quantities:

(1)*b*	*N*	g./l.	oz./gal.
Basic copper carbonate $(Cu^{+II})Cu(OH)_2.CuCO_3$	0.60[1]	33	4.4
Zinc carbonate $ZnCO_3$	0.15	10	1.3
Sodium cyanide (NaCN)	1.85	90	12.0
Required for copper 0.60 + 0.60	= 1.20 *N*		
for zinc 0.15 + 0.15	= 0.30 *N*		
for free cyanide	0.35 *N*		
Total NaCN	1.85 *N*		

[1] This is equivalent to a 0.30 *N* concentration of a cuprous compound, Cu^{+I}.

In a solution so prepared the carbonate will be 0.45 *N*, *i.e.*, about three-fourths that in the first formula. If desired, 7.5 g./l. or 1 oz./gal. of sodium carbonate may be added initially. As however carbonate is continually forming in the solution and tends to reach an undesirable concentration, metal cyanides are preferable to carbonates for replenishing the baths.

For plating on cast iron, a lower content of free cyanide is desirable, *e.g.* about 0.2 *N*, 10 g./l. or 1.3 oz./gal.

The concentrations in the above formulas are suitable for still plating or for mechanical conveyors. For barrel plating

a higher metal content, *e.g.*, 30 g./l. or 4 oz./gal., with the other constituents increased proportionally, is sometimes used, though there is no conclusive evidence that a higher concentration is necessary or desirable.

During operation some ammonia (NH_3) always forms in the solution, and is usually advantageous. In some baths the initial addition of a small amount, *e.g.*, 1 c.c. of aqua ammonia per liter, (or 0.15 fl. oz./gal.) improves the deposits. Further additions of ammonia are usually unnecessary unless the bath has stood unused for some time.

Brass plating solutions are usually operated at slightly elevated temperatures, *e.g.*, 32 to 45°C. (90 to 113°F.). The current density is usually from 0.2 to 0.3 amp./dm.^{2} (2 to 3 amp./sq.ft.). In cold solutions the cathode efficiency is usually below 70 per cent and there is considerable evolution of hydrogen. In warm solutions, especially with fairly high metal content, the cathode efficiency is about 90 per cent. Sufficient free cyanide should be present to keep the anodes clean, otherwise they become coated with zinc cyanide or carbonate. An excessive content of free cyanide decreases the cathode efficiency. Usually the free cyanide content is equivalent to 0.2 to 0.4 that of combined cyanide.

Bronze Plating.—The bronze plating now commonly applied to hardware and similar articles, is not a true bronze (*i.e.* an alloy of copper and tin) but is brass with a high copper content, *e.g.*, 90 to 95 per cent of copper. To deposit such an alloy it is not only necessary to have a high ratio of copper and zinc in the solution, but also a low free cyanide content, which favors the deposition of copper. A typical formula for a bronze plating solution is as follows:

(2)

	N	g./l.	oz./gal.
Copper cyanide (CuCN)	0.33	30	4.0
Zinc cyanide $Zn(CN)_2$	0.033	2	0.3
Sodium cyanide NaCN	0.90	49	6.5
Copper content, Cu	0.33	21	2.85
Zinc content, Zn	0.033	1.1	0.15
Free sodium cyanide, NaCN	0.20	10	1.5

Such a solution may be operated with 90:10 anodes, at a temperature of 40°C. (104°F.) and a current density from 0.2 to 0.4

amp./dm.^{2} (2 to 4 amp./sq.ft.) It is more difficult to maintain a uniform bronze color than a brass, as a slight change in the zinc content of the deposit changes greatly the ratio of the two metals. Practically it has been found that the addition of 7.5 to 15 g./l. (1 to 2 oz./gal.) of Rochelle salt ($KNaC_4H_4O_6.4H_2O$) permits the desired anode corrosion to be obtained with the low free cyanide content required for the above reasons. The production of deposits with a uniform color is thereby aided. When the right concentration of Rochelle salt is present, the solution next to the anodes has a greenish color, while the rest of the solution has a "wine color."

(c) **Methods of Analysis.**—The analysis of brass solutions is quite similar to that of cyanide copper solutions and subject to the same limitations. The metal content can be readily determined. The "free cyanide" can be titrated under constant conditions so as to give approximate results. Carbonate can be determined, but the free alkali is difficult to estimate.

Free Cyanide.—If the operation is carried out as for copper solutions (page 230) the results are less consistent than with other cyanide solutions. This difficulty can be largely overcome by adding to the brass solution sufficient barium nitrate to precipitate all the carbonate, filtering out the barium carbonate, and titrating with silver nitrate in the usual way with potassium iodide present. The presence of free alkali in a brass solution makes the determination and calculation of free cyanide uncertain. By a modification of the method used for zinc cyanide solutions (p. 332) the total cyanide may be approximately determined.

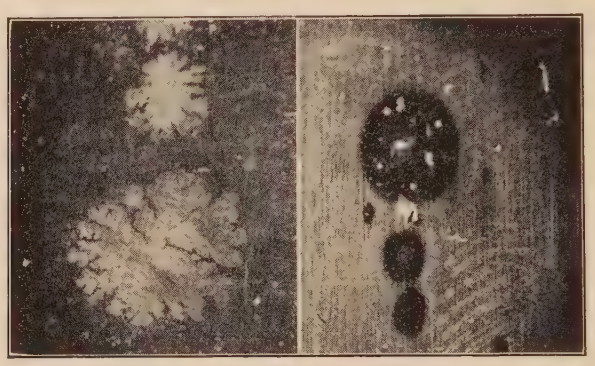
Copper and Zinc.—A 10-c.c. sample is evaporated with sulphuric acid under a hood, hydrocyanic acid expelled, and organic matter destroyed with nitric acid. The solution is diluted, a few drops of nitric acid added, and the copper is determined electrolytically. Five grams of ammonium chloride are added and the solution is made alkaline with ammonia, and any ferric hydroxide is filtered out. It is then neutralized with hydrochloric acid, of which 5 c.c. excess (concentrated) is added. The zinc is then determined volumetrically with ferrocyanide (page 325).

It is also possible to deposit both the copper and zinc from a sample (*e.g.*, 25 c.c.) of the plating solution which has been diluted to 100 c.c. The platinum cathode with the deposit of the two metals is weighed, after which the deposit is dissolved in

nitric acid. This solution is diluted and the copper is deposited from the acid solution. The difference between the two weights represents the zinc content of the solution.

Carbonate.—This may be determined as in copper solutions (page 231).

(d) **Spotting Out.**—Under brass plating may conveniently be considered the defect known as "spotting out," which has proven so troublesome to platers. This subject has recently been investigated at the Bureau of Standards by W. P. Barrows, Research Associate of the American Electroplaters' Society. For details of his research the full report[1] should be consulted. The principal conclusions are as follows.



A B

FIG. 33.—A, Typical Appearance of Crystal Spots on Sulphide Finishes. B, Typical Appearance of Stain Spots Caused by Chemicals Absorbed in Pores.

Under the above term as commonly used, two entirely distinct defects have been included. The first type, which may be designated as "crystal spots," appear as nearly black branching crystals, only on metals with a sulphide ("oxidized") finish, that have been lacquered. These usually require several weeks for their formation. The "stain spots" occur chiefly upon porous cast metals, either lacquered or unlacquered, in the form of irregular discolored stains. These are usually visible after a few days exposure to moist air. The two types are illustrated in Fig. 33.

The crystal spots consist of cuprous sulphide, Cu_2S, the formation of which is caused or accelerated by the presence of sulphur.

[1] Bureau of Standards *Research Paper* 72. *Journ. Research*, vol. 2, p. 1085, 1929.

The latter may come from sulphur in the air, *e.g.*, from sulphur melting pots; from rubber bands; or from wrapping paper or cardboard. The only promising remedies are (*a*) the use of a lacquer found by test to retard the crystal growth; (*b*) the application of a thin film of grease to the lacquered surface, and (*c*) the use of wax paper for wrapping the articles.

The stain spots are far more common, and are encountered especially upon cast iron, brass or bronze that has been plated with copper or brass. The stains are the result of (*a*) the presence of pores in the base metal, (*b*) the inclusion in these pores of chemicals, either acid or alkaline, from the pickling, cleaning or plating solutions; and (*c*) the susbequent absorption by the substances in the pores of moisture from the atmosphere, which causes the compounds to exude or "creep" out and cause stains.

It was found that alkaline compounds are much more likely to cause this spotting, as they are more difficult to rinse out of the pores than acid substances. Subsequent rinsing, however extended, or even treatment with dilute acids, will not entirely remove the alkaline compounds.

The only promising remedies are (*a*) the production of less porous castings, which may sometimes be accomplished by a change in design or in casting methods; (*b*) allowing the articles after plating, to stand in a moist atmosphere for about 24 hours to allow the salts to spot out, after which they are given a final finish and lacquered, and (*c*) the use of a lacquer which has been found by test to retard the stain spotting. In general the phenol condensation lacquers are relatively impervious to moisture and also retard the stain spotting. Recently however, certain kinds of nitrocellulose lacquers have been developed which exert considerable protection against stain spotting.

CHAPTER XXII

EXPERIMENTS IN ELECTRODEPOSITION

Not infrequently platers or electrotypers find it necessary to make certain experiments. Thus, for example, a solution may not be giving a sufficienthly brigired to oveor it may not have good throwing power, and it is dest deposit, rcome these defects. In other instances information is received from another plater, or from some published article, that indicates the possibility of making some improvement in the quality or cost of the plating. In all such cases it is highly desirable to have facilities available for conducting tests upon a small scale upon the same class of material before making any radical changes in the operating tanks. Even when extended laboratory experiments have been made it is not always safe or advisable to attempt to apply the conclusions directly to large-scale commercial operation. This gap between research and practice is not peculiar to electrodeposition. It can be bridged only by intelligent cooperation and through experiments on a semi-commercial scale. The following suggestions refer primarily to such experiments as may be conducted by electroplaters who do not have facilities for making chemical analyses or precise measurements.

(a) **Current Source.**—It is not necessary to use elaborate equipment for this purpose. In most cases it will be possible to secure the necessary current from the plating generator by connecting to some convenient point on the switchboard or the busbars. For many purposes, however, a 6-volt storage battery will prove useful. One or more rheostats can be made from coils of resistance wire. A portable ammeter and voltmeter of appropriate range should be secured. A voltmeter with a range of 0 to 10 volts will usually be suitable. An ammeter with self-contained shunts, and having three scales, *e.g.*, 1, 10, and 50 amp., will permit experiments over a wide range. For such purposes moderate-priced dependable instruments should be secured, but it is not necessary to employ precision instruments. There is practically no case of actual deposition in which an accuracy

greater than 5 per cent in the voltage or current has any significance. It is seldom possible to fix the distance between anode and cathode within 5 per cent, *e.g.*, 1/4 in. in 5 in., or to measure the actual or effective cathode area within 5 per cent.

(b) **Containers.**—For volumes up to 5 gal. (20 l.) glass storage battery jars are very convenient. For volumes from 5 to 25 gal. (20 to 100 l.) stoneware crocks or tanks are most frequently used. Cylindrical crocks are cheap and are usually available. They have the disadvantage that the circular cross-section does not permit spacing the electrodes similarly to their position in a large tank. For this reason rectangular stoneware or enameled iron tanks are often preferable. Acid-proof or chemical stoneware, glass, and enamel have the advantage over wood in that they can be completely cleaned and hence can be used at different times for various kinds of solutions without danger of contamination. Often it is convenient to build a wooden tank of the same cross-section but shorter in length than the regular tank. Thus a tank 32 × 12 × 32 in. deep will have just one-sixth the capacity of a tank 32 × 72 × 32 in. deep, and may nearly reproduce the conditions of the larger tank.

(c) **Series Connections.**—In practically every experiment the purpose is to obtain a *comparison* of the behavior or properties of two or more solutions. Whenever this is feasible, most reliable results are secured by operating the tanks in series rather than in parallel. In this way the same current must necessarily flow through all tanks, and if the anode and cathode areas are the same in the two tanks, the current densities must be equal. Not infrequently erroneous conclusions are drawn from a comparison of two solutions in parallel, in which case, if the resistances or polarizations differ, the current densities vary, and hence one deposit may be produced at a higher current density than the other. Even if, as must be admitted, the voltage or "pressure" to be used on the tanks is more easily controlled in practice than the current density, the favorable voltage can usually be determined from measurements on the tanks in series. One practical objection to conducting experiments in series is that if a potential of only 6 volts is available from the generator, this may not be sufficient to produce the desired current density in two series tanks. If a three-wire system with 6 to 12 volts is available, the higher voltage can be secured by connecting with the outer terminals. If the experiments can be conducted outside the regular

hours, even a 6-volt generator may furnish the small currents desired, because as high as 8 volts can be secured by adjusting the field rheostat.

(d) **Cathode Efficiency.**—Except so far as the appearance or structure of the deposit is thereby affected, the plater is rarely concerned with small differences in current efficiency. If, as is usually the case, the actual cost of the current is only a few per cent of the cost of the plating operation, a difference of 5 per cent in cathode efficiency has little effect upon operating costs unless the work is being conducted upon a very large scale. Silver and gold are practically the only metals of which the thickness (or weight per piece) is usually specified. With all metals there are certain to be much greater variations than 5 per cent in thickness on different pieces or on different parts of the same piece.

It is doubtful, therefore, whether the plater is often justified in computing the cathode efficiency in his experiments. To do so accurately requires the use of a sensitive balance, such as may also be used for approximate analytical work. The cathode efficiency should be measured by comparison with a copper coulometer (page 62), or, for very accurate work, a silver coulometer. Measurement of the quantity of electricity, by observing the ammeter reading and the time, is subject to considerable uncertainty, not so much from actual errors in the ammeter calibration and in observing the time, as in the fluctuations in current that are likely to occur. Measurement of the thickness by a micrometer has little value as an indication of current efficiency, as the metal is never uniformly distributed. It is useful, however, in indicating what thickness may be expected on a similarly shaped article under the same conditions.

In order to measure the cathode efficiency of a solution, it is necessary to clean, dry, and weigh the cathode and also a copper cathode for the coulometer. The electrodes in the coulometer should have such an area that the current density is not more than 1 amp./dm.^{2} (9.3 amp./sq. ft.) in agitated copper solutions, or 0.5 amp./dm.^{2} (4.6 amp./sq.ft.) in still solutions. If, therefore, in the plating experiments a cathode current density of 2 amp./dm.^{2} (19 amp./sq.ft.) is used, the coulometer anode and cathode should have for agitated copper solutions an area twice as great as the cathodes in the plating bath, and for a still copper solution, four times as great. It is preferable in such experiments

to use plain sheet metal for the cathode, rather than an article of irregular shape. Even with a plain sheet there is considerable difference in current density between the center and edges, and on irregular shapes there are still greater differences. The efficiency obtained on an irregular-shaped piece is simply the average of the efficiencies at the various current densities existing on the article and is therefore not an index of current efficiency at any given current density. In some cases it may prove practicable to clean and dry ten small articles, to weigh them on a fairly accurate balance, and, by reweighing after plating, to determine the weight of the metal deposited by a definite current in a given time. The current efficiency can then be calculated very roughly.

(e) **Anode Efficiency.**—Instead of determining the anode efficiency by loss of weight, it is usually more satisfactory to observe any changes in the metal content or acidity of the solutions. We are not usually so much concerned with securing 100 per cent anode efficiency as in having the anode efficiency equal to the cathode efficiency. If the solution is adjusted to the same height in the vessel to make up for evaporation, and if mechanical losses are reduced to a minimum, a decrease in specific gravity will serve as an indication of low anode efficiency. Any increase in acidity is an even more sensitive sign of relatively poor anode efficiency. This can be determined by direct titration in acid solutions, or by measuring the pH of nearly neutral solutions. Alkaline solutions are less easily tested for pH or total alkalinity, owing to the complications caused by the formation of carbonates, etc.

(f) **Comparisons.**—Of greater importance than the current efficiency is the character of the deposit produced at different current densities or temperatures, or in solutions of different composition. Experiments upon the composition of the solution may be made for the purpose of determining the best addition to make to some bath which is not giving satisfaction. In such a case all that is necessary is to place in each of two small tanks a definite volume (*e.g.*, 5 gal.) of the solution from the tank and to make to one tank successive additions of the substance whose effects are to be studied, until the desired deposit is secured, or else it becomes obvious that the addition of this substance is either useless or detrimental. In the latter case it is usually better to throw away this 5 gal. of solution than to attempt to

make additions of other substances to it. A careful record of all additions should be made and all the essential conditions and results should be noted. Too much stress cannot be laid upon the importance of changing only one variable at a time. If a comparison is made of a still bath at ordinary temperature with an agitated solution at elevated temperature, and containing additional acid, it is impossible to determine the cause of any differences that may be observed in the deposits. When it is found that a certain addition, *e.g.*, 0.5 oz./gal. of sodium chloride to a 5-gal. jar of a nickel bath, produces a decided improvement, it is easy to calculate and add the corresponding amount to the large bath.

When it is desired to study different types of baths and to determine the effect of various concentrations or conditions, it is preferable to conduct preliminary experiments upon a still smaller scale, *e.g.*, 1 gal., or even 1 qt. This is especially helpful if no chemical analyses are available. It is very much cheaper to make up from definite amounts of the same materials as are to be used on a large scale, a fresh sample of a bath for every new series of tests, than to have it analyzed. Wherever possible, such analyses should be made for the purpose of detecting changes in composition, but not in order to save the expense of a small volume of solution. On the other hand, it may be very misleading to prepare a certain solution, operate it for several days, make additions to it, and again operate it, on the assumption that the composition has not changed except through the additions. Whatever conclusions are reached from small-scale experiments should be confirmed by a few tests on a semi-commercial scale, *e.g.*, 10 gallons over a longer period.

(g) **Chemical Equivalents.**—In studying the effects of similar substances, consideration should be given to their chemical equivalents. Thus a comparison of two solutions to which have been added respectively 2 oz./gal. (15 g./l.) of sodium chloride (NaCl) and of magnesium chloride ($MgCl_2.6H_2O$) is no indication of the relative value of the metals sodium and magnesium, as the solutions then contain quite different amounts of chlorine. As the equivalent weight of sodium chloride is 58.5 and that of magnesium chloride is $203/2 = 101.5$, it is necessary to use about 1.75 times as much magnesium chloride as of sodium chloride to produce solutions with the same chlorine content, thus 2 oz./gal. (15g/l) of NaCl and 3.5 oz./gal. (26 g/l) of

$MgCl_2.6H_2O$. A rough calculation of the equivalent weights of the substances concerned will indicate the relative proportions to be employed. Failure to consider the equivalent strengths or normalities of solutions has often led to confusing or anomalous results. If the substances are not definite compounds, or if they are of entirely different constitution, there is no special advantage in computing the equivalent weights, and, indeed, this is not always possible. Thus a comparison of the effect of glue, licorice, and corn syrup as addition agents in a zinc solution must be on an entirely empirical basis, and will usually involve quite different concentrations.

(h) **Scope of Experiments.**—Before starting any series of experiments it is well to consider first what properties of the solution it is especially desired to improve, aud secondly what conditions or additions are likely to effect such a change. A tentative schedule or skeleton outline of experiments may then be prepared. By such a plan the number of experiments required may be restricted and the best order may be determined in advance. It is usually preferable to conduct experiments at first over fairly wide limits for each variable. If then only a slight change in behavior is noted at the extremes used, it is generally safe to assume that the results with intermediate conditions will be between these extremes. If, however, it is found that at one extreme as first selected, a very poor result is secured, an outside limit to that condition is then definitely established.

Among the factors that can most readily be controlled and studied are (1) current density, (2) temperature, (3) metal salt concentration, (4) acidity, (5) anode corrosion and (6) conductivity. Suppose that a nickel bath containing nickel sulphate *N*, sodium chloride 0.1 *N*, and boric acid 0.1 *N*, and with a pH of 5 (colorimetric corrected) is being operated at ordinary temperature (about 20°C., or 68°F.) with 4 volts on the tank, at a current density of 0.5 amp./dm.^{2} (5 amp./sq. ft.), and is causing difficulty with cracked deposits on brass. It is desired to make a few experiments to determine what remedy to apply. We might then study the deposition over the following range of conditions:

(1) Current density: 0.25 and 1 amp./dm.^{2} (2.5 and 10 amp./sq. ft.).
(2) Temperature: 30° and 50°C. (86 and 122°F.).

(3) Nickel concentration: 0.5 *N* secured by diluting the solution with an equal volume of water; and 1.5 *N*, obtained by adding additional nickel sulphate.
(4) Sodium chloride concentration: increased to 0.2 and 0.4 *N* by addition of sodium chloride, to increase anode corrosion.
(5) Acidity from pH 4, secured by careful addition of sulphuric acid, to pH 6, by the addition of ammonia.
(6) Conductivity increased by addition of sodium sulphate. and also the sodium chloride in (4).

As apart from any direct evidence to the contrary, any of the above changes might produce an improvement or the reverse in the deposit, the danger and futility of making arbitrary changes in the operating tanks are very obvious. It is equally true that time and facilities would not usually permit carrying out as many experiments as are here suggested. It is therefore necessary for the plater to use his experience and judgment in determining which of the factors should be first studied. On general principles he would naturally try the effect of reducing the current density. Similarly, he can predict that warming the solutions will decrease the tendency toward cracking of deposits. Likewise an increase in pH by addition of ammonia will usually be helpful in such a case. If then a decided improvement is made in these three conditions by changing one at a time, on a small scale, he is entirely justified in applying the corresponding change to the large tanks. If then he finds that after a few days the pH of his solution decreases, *i.e.*, it is becoming acid, it is at least an indication that anode corrosion is inadequate. This may be remedied by cleaning the anodes, increasing the anode area, or by the addition of chloride to the bath. The effect of increasing the chloride content should be determined first on a small scale, and operated for at least a few days.

(i) **Records.**—In making such experiments it is important to keep careful records, not only for the purpose of drawing proper conclusions at that time, but also of permitting comparisons to be made at some future time. This record should also include the effect of the changes subsequently made in the operating tanks. No set form will meet all requirements, but a simple report blank can be mimeographed and used to great advantage. Even in those cases where it is not necessary to

record complete data, the presence of the appropriate blank spaces serves as a reminder to decide whether the observations should be made. In a series of similar experiments it is often sufficient to note the specific change in conditions and to refer to the preceding experiment for other details. Where chemical analyses are available, a suitable space should be left on the card for recording the results. A simple form which has been found useful is shown on page 398.

REPORT FORM

Plating Experiments

Experiment No. *102* Date *February 1, 1920*

Subject *Nickel solution* Topic *Plating reflectors*

Purpose *Remedy for cracking*

SOLUTION

Constituent	Original Formula g./l.	oz./gal.
Nickel sulphate	*16*	
Ammonium chloride	*1*	
Boric acid	*2*	
	Addition	
Ammonium chloride	*1*	

Analysis Original

After addition

Volume *2 gal.*
Sp. gr. *1.08*
Temp. *75°F.*
Appear. begin. *Clear*
end *Yellow ppt.*
pH *5.0* (colorimetric corrected)
Resistivity ohm-cm. 25

CURRENT

Amperes *9*

Amp./sq. ft.
Anode *9*
Cathode *12*
Time *45 min.*
Voltage *4.2*

CATHODES

Number *1* Size *8 in. diam. 4 in. deep*
Shape *Oval reflector*—Approx. area *0.75 sq. ft.*
Material *Brass*
Preparation *Electrolytic cleaner*

Deposit appear. *White and free of cracks*

ANODES

Number *4*
Size *3 × 2 × 6 in.*
Shape *Elliptical*
Composition *99% Ni*
Distance from cathode *4 in.*

Cathode efficiency:

	Cathode	Copper
2nd. wt.	*208.63*	*70.45 g.*
1st wt.	*201.23*	*62.15*
Increase	*7.40*	*8.30*
Amp. hr.		*7*

Wt. *Ni.* calc. from wt. Cu. *7.67*
Cathode eff. *96.5%*

REMARKS

The deposit was decidedly better than that obtained in Expt. 101 with solution from tank. Indicates that addition of 1 oz./gal. of ammonium chloride to the large bath will be helpful. Feb. 2—An addition of 20 lb. (1 oz./gal.) of ammonium chloride was made to tank No. 2 (320 gal). Feb. 4—No further difficulty has been observed with cracking. The pH of the solution has increased from 5.0 to 5.4, indicating better anode corrosion.

Signed

APPENDIX

TABLE 1.—CONVERSION OF CENTIGRADE (C.) TO FAHRENHEIT (F.) TEMPERATURES

°C. °F.	°C. °F.	°C. °F.	°C. °F.
0 = 32	30 = 86	55 = 131	80 = 176
5 = 41	35 = 95	60 = 140	85 = 185
10 = 50	40 = 104	65 = 149	90 = 194
15 = 59	45 = 113	70 = 158	95 = 203
20 = 68	50 = 122	75 = 167	100 = 212
25 = 77			

TABLE 2.—CONVERSION OF FAHRENHEIT (F.) TO CENTIGRADE (C.) TEMPERATURES

°F. °C.	°F. °C.	°F. °C.	°F. °C.
0 = − 17.8	55 = 12.8	110 = 43.3	165 = 73.9
5 = − 15.0	60 = 15.6	115 = 46.1	170 = 76.7
10 = − 12.2	65 = 18.3	120 = 48.9	175 = 79.4
15 = − 9.4	70 = 21.1	125 = 51.7	180 = 82.2
20 = − 6.7	75 = 23.9	130 = 54.4	185 = 85.0
25 = − 3.9	80 = 26.7	135 = 57.2	190 = 87.8
30 = − 1.1	85 = 29.4	140 = 60.0	195 = 90.6
32 = 0.0	90 = 32.2	145 = 62.8	200 = 93.3
35 = 1.7	95 = 35.0	150 = 65.6	205 = 96.1
40 = 4.4	100 = 37.8	155 = 68.3	210 = 98.9
45 = 7.2	105 = 40.6	160 = 71.1	212 = 100.0
50 = 10.0			

TABLE 3.—CONVERSION OF DEGREES BAUMÉ (BÉ.)[1] TO SPECIFIC GRAVITY (SP. GR.)

°Bé. Sp. gr.	°Bé. Sp. gr.	°Bé. Sp. gr.	°Bé. Sp. gr.	°Bé. Sp. gr.
0 = 1.000	8 = 1.058	16 = 1.124	24 = 1.198	32 = 1.283
1 = 1.007	9 = 1.066	17 = 1.133	25 = 1.208	33 = 1.295
2 = 1.014	10 = 1.074	18 = 1.142	26 = 1.218	34 = 1.306
3 = 1.021	11 = 1.082	19 = 1.151	27 = 1.229	35 = 1.318
4 = 1.028	12 = 1.090	20 = 1.160	28 = 1.239	36 = 1.330
5 = 1.036	13 = 1.098	21 = 1.169	29 = 1.250	37 = 1.343
6 = 1.043	14 = 1.107	22 = 1.179	30 = 1.261	38 = 1.355
7 = 1.051	15 = 1.115	23 = 1.189	31 = 1.272	39 = 1.368
				40 = 1.381

TABLE 4.—CONVERSION OF SPECIFIC GRAVITY (SP. GR.) TO DEGREES BAUMÉ (BÉ.)[2]

Sp. gr. °Bé	Sp. gr. °Bé	Sp. gr. °Bé	Sp. gr. °Bé	Sp. gr. °Bé
1.00 = 0.00	1.08 = 10.7	1.16 = 20.0	1.24 = 28.1	1.32 = 35.2
1.01 = 1.44	1.09 = 12.0	1.17 = 21.1	1.25 = 29.0	1.33 = 36.0
1.02 = 2.84	1.10 = 13.0	1.18 = 22.1	1.26 = 29.9	1.34 = 36.8
1.03 = 4.22	1.11 = 14.4	1.19 = 23.2	1.27 = 30.8	1.35 = 37.6
1.04 = 5.58	1.12 = 15.5	1.20 = 24.2	1.28 = 31.7	1.36 = 38.4
1.05 = 6.90	1.13 = 16.7	1.21 = 25.2	1.29 = 32.6	1.37 = 39.2
1.06 = 8.21	1.14 = 17.8	1.22 = 26.2	1.30 = 33.5	1.38 = 39.9
1.07 = 9.5	1.15 = 18.9	1.23 = 27.1	1.31 = 34.3	1.39 = 40.7
				1.40 = 41.4

[1] This scale for liquids heavier than water is defined by the formula: Baumé $= 145 - \frac{145}{\text{Sp. gr. } \frac{60°}{60°} \text{F.}}$, where sp. gr. $\frac{60°}{60°}$ F represents the specific gravity of the solution at 60°F. referred to water at 60°F.

[2] Tables 3 and 4 are given in more complete and accurate form in Circular No. 19 of the Bureau of Standards.

TABLE 5.—APPROXIMATE EQUIVALENTS OF METRIC AND CUSTOMARY UNITED STATES UNITS

Length:		
1 meter (m.)	=	39.37 in.
1 decimeter (dm.)	=	3.937 in.
1 centimeter (cm.)	=	0.3937 in.
1 inch (in.)	=	2.54 cm.
1 foot (ft.)	=	30.48 cm.
Area:		
1 square meter ($m.^2$)	=	1,550 sq. in.
1 square decimeter ($dm.^2$)	=	15.5 sq. in.
1 square centimeter ($cm.^2$)	=	0.155 sq. in.
1 square inch (sq. in.)	=	6.45 $cm.^2$
1 square foot (sq. ft.)	=	9.29 $dm.^2$
Volume:		
1 cubic meter ($m.^3$)	=	35.31 cu. ft.
1 cubic decimeter ($dm.^3$)	=	61.02 cu. in.
1 cubic centimeter ($cm.^3$ or c.c.)	=	0.061 cu. in.
1 cubic inch (cu. in.)	=	16.39 $cm.^3$
1 cubic foot (cu. ft.)	=	28.32 $dm.^3$
Capacity (liquid measure):		
1 liter (l.)	=	1,000 ml. (or about 1,000 c.c.)
1 liter	=	1.057 qt.
1 milliliter[1] (ml.) or c.c.	=	0.034 fluid oz.
1 gallon[2] (gal.)	=	231 cu. in.
1 gallon	=	3.785 liters
1 quart (qt.)	=	0.946 liters
1 fluid ounce (fl. oz.)	=	29.4 ml. or c.c.
Mass (weight):		
1 kilogram (kg.)	=	1,000 g.
1 kilogram	=	2.205 avoirdupois lb.
1 gram (g.)	=	0.0353 avoirdupois oz.
1 gram	=	0.0322 troy oz.
1 avoirdupois ounce (oz.)	=	28.35 g.
1 avoirdupois pound (lb.)	=	453.6 g.
1 troy ounce (tr. oz.)	=	31.10 g.

1 liter of water weighs 1,000 g.

[1] The milliliter, the true unit of capacity, is at present commonly designated (*e.g.*, on volumetric apparatus) as a cubic centimeter (usually abbreviated $cm.^3$ or c.c.), from which, however, it has a slightly different value. For all practical purposes, however, the term "cubic centimeter" and the abbreviation c.c. may be employed.

[2] One British Imperial gallon is equal to the volume at 62°F. of 10 lb. of water. It is equivalent to 277.41 cu. in., to 4.55 liters, or to 1.20 U. S. gallons. Therefore to convert oz./U. S. gal. to oz./Imp. gal., multiply by 1.2.

TABLE 6.—APPROXIMATE CONVERSION FACTORS FOR METRIC AND CUSTOMARY UNITED STATES UNITS

1. Grams per liter (g./l.) multiplied by 0.134 = avoirdupois ounces per gallon[1] (oz./gal.).

2. Avoirdupois ounces per gallon (oz./gal.) multiplied by 7.5 = grams per liter[2] (g./l.).

3. Grams per liter (g./l.) multiplied by 0.122 = troy ounces per gallon (tr. oz./gal.).

4. Troy ounces per gallon (tr. oz./gal.) multiplied by 8.2 = grams per liter (g./l.).

5. Grams per liter (g./l.) multiplied by 2.44 = pennyweights per gallon (dwt./gal.).

6. Pennyweights per gallon (dwt./gal.) multiplied by 0.41 = grams per liter (g./l.).

7. Grams per liter (g./l.) = ounces per cubic foot (oz./cu. ft.).

8. $\frac{\text{grams per liter}}{\text{10 multiplied by specific gravity}}$ = percentage by weight.

9. Amperes per square decimeter (amp. dm.^{2}) multiplied by 9.29 = amperes per square foot (amp./sq. ft.).

10. Amperes per square foot (amp./sq. ft.) multiplied by 0.108 = amperes per square decimeter (amp./dm.^{2}).

11. Kilograms per square centimeter (kg./cm.^{2}) (as in tensile strength) multiplied by 14.22 = pounds per square inch (lb./sq. in.).

12. Pounds per square inch (lb./sq. in.) multiplied by 0.0704 = kilograms per square centimeter (kg./cm.^{2}).

13. Grams per square decimeter (g./dm.^{2}) multiplied by 0.328 = ounces per square foot (oz./sq. ft.).

14. Ounces per square foot (oz./sq. ft.) multiplied by 3.04 = grams per square decimeter (g./dm.^{2}).

15. Cubic centimeters per liter (c.c./l.) multiplied by 0.129 = fluid ounces per gallon (fl. oz./gal.).

16. Fluid ounces per gallon (fl. oz./gal.) multiplied by 7.7 = cubic centimeters per liter (c.c./l.).

17. Specific gravity of a metal divided by 12 = oz./sq. ft. for 0.001 in.

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[1] 1a. Grams per liter (g./l.) multiplied by 0.161 = avoirdupois ounces per British Imperial gallon (av. oz./Imp. gal.).

[2] 2a. Avoirdupois ounces per Imperial gallon (av. oz./Imp. gal.) multiplied by 6.2 = grams per liter (g./l.).

TABLE 7.—ATOMIC WEIGHTS OF COMMON ELEMENTS[1] (1929)

	Symbol	Atomic weight		Symbol	Atomic weight
Aluminum	Al	26.97	Lithium	Li	6.94
Antimony	Sb	121.77	Magnesium	Mg	24.32
Arsenic	As	74.96	Manganese	Mn	54.93
Barium	Ba	137.36	Mercury	Hg	200.61
Bismuth	Bi	209.00	Molybdenum	Mo	96.0
Boron	B	10.82	Nickel	Ni	58.69
Bromine	Br	79.92	Nitrogen	N	14.008
Cadmium	Cd	112.41	Oxygen	O	16.00
Calcium	Ca	40.07	Phosphorus	P	31.02
Carbon	C	12.00	Platinum	Pt	195.23
Chlorine	Cl	35.46	Potassium	K	39.10
Chromium	Cr	52.01	Silicon	Si	28.06
Cobalt	Co	58.94	Silver	Ag	107.88
Copper	Cu	63.57	Sodium	Na	23.00
Fluorine	F	19.00	Strontium	Sr	87.63
Gold	Au	197.2	Sulphur	S	32.06
Hydrogen	H	1.008	Tin	Sn	118.70
Iodine	I	126.93	Tungsten	W	184.0
Iron	Fe	55.84	Zinc	Zn	65.38
Lead	Pb	207.22			

[1] From report of International Committee on Atomic Weights, 1929.

For most calculations in electroplating, the nearest whole numbers may be employed.

TABLE 8.—USUAL VALENCES OF COMMON ELEMENTS

Name	Symbol	Valence	Type of compound
Aluminum	Al	+ III	Aluminum salt and aluminate
Antimony	Sb	+ III	Antimonite
		+ V	Antimonate
Arsenic	As	+ III	Arsenite
		+ V	Arsenate
Barium	Ba	+ II	Barium salt
Boron	B	+ III	Borate
Cadmium	Cd	+ II	Cadmium salt
Calcium	Ca	+ II	Calcium salt
Carbon	C	+ IV	Carbonate
Chlorine	Cl	− I	Chloride
		+ V	Chlorate
		+ VII	Perchlorate
Chromium	Cr	+ II	Chromous salt
		+ III	Chromic salt
		+ VI	Chromate
Cobalt	Co	+ II	Cobaltous salt
		+ III	Cobaltic salt
Copper	Cu	+ I	Cuprous salt
		+ II	Cupric salt
Fluorine	F	− I	Fluoride
Gold	Au	+ I	Aurous salt
		+ III	Auric salt
Hydrogen	H	+ I	Hydride
Iodine	I	− I	Iodide
Iron	Fe	+ II	Ferrous salt
		+ III	Ferric salt

TABLE 8.—USUAL VALENCES OF COMMON ELEMENTS (CONTINUED)

Name	Symbol	Valence	Type of Compound
Lead	Pb	+ II	Lead salt
Magnesium	Mg	+ II	Magnesium salt
Manganese	Mn	+ II	Manganous salt
		+ VII	Permanganate
Mercury	Hg	+ I	Mercurous salt
		+ II	Mercuric salt
Nickel	Ni	+ II	Nickelous salt
		+ III	Nickelic salt
Nitrogen	N	− III	Ammonia; Ammonium salt
		+ III	Nitrite
		+ V	Nitrate
Oxygen	O	− II	Oxide
Phosphorus	P	+ III	Phosphite
		+ V	Phosphate
Platinum	Pt	+ IV	Platinum salt
Potassium	K	+ I	Potassium salt
Silicon	Si	+ IV	Silicate
Silver	Ag	+ I	Silver salt
Sodium	Na	+ I	Sodium salt
Sulphur	S	− II	Sulphide
		+ IV	Sulphite
		+ VI	Sulphate
Tin	Sn	+ II	Stannous salt; Stannite
		+ IV	Stannic salt; Stannate
Zinc	Zn	+ II	Zinc salt

TABLE 9.—ELECTROCHEMICAL EQUIVALENTS[1]

	Weight per unit area		Valence	Electrochemical equivalent			Thickness		Amp.-hr. per dm.² to deposit 0.1 mm.	Amp.-hr. per sq. ft. to deposit 0.001 in.
	g./dm.² for 0.1 mm. = sp. gr.	oz./sq. ft. for 0.001 in.		mg./coulomb	g./amp.-hr.	oz./100 amp.-hr.	mm. for 1 amp.-hr. per dm.²	in. for 100 amp.-hr. per sq. ft.		
Antimony	6.7	0.56	3	0.415	1.495	5.3	0.0223	0.0095	4.48	10.6
Arsenic	5.7	0.47	3	0.259	0.932	3.3	0.0164	0.0069	6.12	14.4
Cadmium	8.6	0.71	2	0.582	2.097	7.4	0.0244	0.0103	4.10	9.7
Chromium	7.1	0.59	3	0.180	0.647	2.3	0.0091	0.0039	10.95	25.9
			6	0.090	0.323	1.1	0.0046	0.0019	21.90	51.8
Cobalt	8.9	0.74	2	0.306	1.100	3.9	0.0124	0.0052	8.09	19.1
Copper	8.9	0.74	1	0.659	2.372	8.4	0.0267	0.0113	3.75	8.8
			2	0.329	1.186	4.2	0.0133	0.0056	7.50	17.7
Gold	19.3	1.44[2]	1	2.044	7.357	23.6[2]	0.0381	0.0162	2.63	6.2
			3	0.681	2.452	7.9[2]	0.0127	0.0054	7.94	18.7
Iron	7.9	0.65	2	0.289	1.042	3.7	0.0132	0.0056	7.58	17.9
Lead	11.3	0.94	2	1.074	3.865	13.6	0.0342	0.0145	2.92	6.9
Nickel	8.9	0.74	2	0.304	1.095	3.9	0.0126	0.0053	7.95	18.7
Platinum	21.4	1.60[2]	4	0.506	1.821	5.8[2]	0.0085	0.0036	11.70	27.7
Silver	10.5	0.79[2]	1	1.118	4.025	12.9[2]	0.0383	0.0163	2.61	6.2
Tin	7.3	0.61	2	0.615	2.214	7.8	0.0303	0.0129	3.30	7.8
			4	0.307	1.107	3.9	0.0152	0.0064	6.60	15.6
Zinc	7.1	0.59	2	0.339	1.219	4.3	0.0172	0.0073	5.82	13.7

[1] It should be emphasized that all of these values are based on 100 per cent current efficiency. In applying them it is necessary to take into account the actual cathode efficiencies. For most metals such as copper, nickel, zinc and silver, the cathode efficiencies are usually over 90 per cent. In such cases the errors involved in using this table directly are no greater than the probable uncertainties in measuring the current densities. However in depositing chromium from chromic acid, in which the valence of chromium is six, the average cathode efficiency is only about 14 per cent. It is therefore necessary to divide the above weights and thickness for Cr^{vi} by 7, or to multiply the periods by 7. The results are then only an approximation.

[2] Troy ounces.

TABLE 10.—ELECTROMOTIVE SERIES[1]

Approximate single potentials of metals toward solutions with normal metal ion concentration or activity. Based on the normal hydrogen electrode as zero.

	Volts		Volts
Zinc	−0.76	*Hydrogen*	0.00
Chromium	−0.6	Antimony	+0.19
Iron (ferrous)	−0.43	Arsenic	+0.32
Cadmium	−0.40	Bismuth	+0.33
Cobalt	−0.29	Copper	+0.34
Nickel	−0.23	Mercury	+0.78
Tin (stannous)	−0.14	Silver	+0.80
Lead	−0.12	Gold	+1.00

[1] Many of these values are at best uncertain, owing in some cases to difficulty in measuring the potentials, and in others to uncertainty as to the metal ion concentration or activity in the solution used. The order in which they are arranged is probably correct, although the relative positions of cadmium and iron are in question

These values refer only to metals in the "active" state. Where they are passive (p. 73) their potentials are more positive. Under most conditions chromium and nickel are passive and their potentials are much more positive than those in this table.

TABLE 11.—RESISTIVITIES[1] OF SOLUTIONS AT 25°C. (77°F.), IN OHM-CM.

Name	Formula	Concentration		
		N	0.5 *N*	0.1 *N*
Hydrochloric acid	HCl	3.01	5.54	26
Sulphuric acid	H_2SO_4	4.81	9.28	40
Hydrofluoric acid	HF	.....	81	280
Acetic acid	$HC_2H_3O_2$	670	870	1,900
Boric acid[2]	H_3BO_3	70,000	220,000	
Chromic acid[2]	H_2CrO_4	3.18	5.81	27
Potassium hydroxide	KOH	5.07	9.48	46
Potassium chloride	KCl	8.94	17.1	78
Potassium cyanide	KCN	8.21	15.3	70
Sodium hydroxide	NaOH	5.77	10.6	50
Sodium chloride	NaCl	11.6	21.7	92
Sodium fluoride	NaF	18.5	29.4	121
Sodium sulphate	Na_2SO_4	16.8	29.1	109
Sodium carbonate	Na_2CO_3	19.1	31.3	117
Sodium phosphate	Na_2HPO_4	31.5	52.4	199
Ammonium hydroxide	NH_4OH	970	1,280	2,700
Ammonium chloride	NH_4Cl	9.34	17.4	78
Ammonium sulphate	$(NH_4)_2SO_4$	12.8	23.0	94
Calcium chloride	$CaCl_2$	12.9	23.8	101
Magnesium sulphate	$MgSO_4$	29.9	49.5	171
Copper sulphate	$CuSO_4$	34.1	56	191
Zinc sulphate	$ZnSO_4$	33.2	53	187
Zinc chloride	$ZnCl_2$	13.4	22.6	101
Cadmium sulphate	$CdSO_4$	36.6	62	210
Cadmium chloride	$CdCl_2$	40.1	58	185
Ferrous chloride	$FeCl_2$	16.5	28.7	
Ferrous sulphate	$FeSO_4$	33.6	53	180
Ferrous ammonium sulphate	$FeSO_4.(NH_4)_2SO_4$	12.0		
Nickel sulphate	$NiSO_4$	33.8	53	195
Nickel ammonium sulphate	$NiSO_4.(NH_4)_2SO_4$	.....	19.5	71
Nickel chloride	$NiCl_2$	14.1	25.0	105
Cobalt sulphate	$CoSO_4$	34.1	57	204
Cobalt chloride	$CoCl_2$	14.5	25.3	75
Silver potassium cyanide	$KAg(CN)_2$	.....	16.0	
Lead fluoborate	$Pb(BF_4)_2$	9.2		

[1] Some of these have been compiled by L. D. Hammond from various sources; others have been computed from International Critical Tables, vol. VI. Certain values have been computed from data at 18°, using known or assumed temperature coefficients. These values are probably correct to about 1 per cent.

[2] Concentrations of boric acid and chromic acid are *M*.

TABLE 12.—HYDROGEN OVERVOLTAGE ON METALS[1]

At 1 amp./dm.^{2} (9.3 amp./sq. ft.) at 25°C. (77°F.)

(Derived from data of Knobel, Kaplan and Eiseman, *Trans. Am. Electrochem. Soc.*, vol. 43, p. 55, 1923.)

METAL	HYDROGEN OVERVOLTAGE VOLTS
Platinized platinum	0.030
Smooth platinum	0.068
Gold	0.390
Electrolytic iron	0.557
Copper	0.584
Brass	0.646
Carbon	0.700
Zinc	0.746
Nickel	0.747
Silver	0.762
Graphite	0.779
Aluminum	0.826
Tin	1.077
Lead	1.090
Cadmium	1.134

[1] These values are simply illustrative. The actual numerical values for any metal depend on the surface condition, the current density, and the solution used. Even the order of the metals is not constant.

TABLE 13.—TOTAL CONCENTRATIONS OF COPPER SULPHATE PLUS SULPHURIC ACID IN SOLUTIONS OF GIVEN SPECIFIC GRAVITY

Specific gravity at $\frac{25°}{4°}$ C.[1]	Copper sulphate plus sulphuric acid		Specific gravity at $\frac{25°}{4°}$ C.[1]	Copper sulphate plus sulphuric acid	
	g./l.	oz./gal.		g./l.	oz./gal.
1.01	20	2.7	1.13	217	29.1
1.02	36	4.8	1.14	234	31.3
1.03	52	7.0	1.15	251	33.6
1.04	68	9.1	1.16	268	35.9
1.05	84	11.3	1.17	286	38.3
1.06	100	13.4	1.18	303	40.6
1.07	117	15.7	1.19	321	43.0
1.08	133	17.8	1.20	339	45.4
1.09	150	20.0	1.21	357	47.8
1.10	166	22.3	1.22	375	50.2
1.11	183	24.5	1.23	393	52.6
1.12	200	26.8			

[1] The specific gravity determined at 25°C. (77°F.) based upon the density of water at 4°C. (39.2°F.).

TABLE 14.—SPECIFIC GRAVITY OF CHROMIC ACID SOLUTIONS AS A FUNCTION OF THE CrO_3 CONTENT[1]

Density $\left(\frac{15°}{4°}\text{ C.}\right)$	CrO_3 content			Density $\left(\frac{15°}{4°}\text{ C.}\right)$	CrO_3 content		
	Molarity	g./l.	oz./gal.		Molarity	g./l.	oz./gal.
1.01	0.15	15	2.0	1.18	2.57	257	34.4
1.02	0.29	29	3.9	1.19	2.72	272	36.4
1.03	0.43	43	5.8	1.20	2.88	288	38.6
1.04	0.57	57	7.6	1.21	3.01	301	40.3
1.05	0.71	71	9.5	1.22	3.16	316	42.3
1.06	0.85	85	11.4	1.23	3.30	330	44.2
1.07	1.00	100	13.4	1.24	3.45	345	46.2
1.08	1.14	114	15.3	1.25	3.60	360	48.2
1.09	1.29	129	17.3	1.26	3.75	375	50.2
1.10	1.43	143	19.1	1.27	3.90	390	52.2
1.11	1.57	157	21.0	1.28	4.06	406	54.5
1.12	1.71	171	22.9	1.29	4.22	422	56.5
1.13	1.85	185	24.8	1.30	4.38	438	58.7
1.14	2.00	200	26.8	1.31	4.53	453	60.7
1.15	2.15	215	28.8	1.32	4.68	468	62.7
1.16	2.29	229	30.6	1.33	4.84	484	64.8
1.17	2.43	243	32.6	1.34	5.00	500	67.0

[1] From data compiled by J. A. Beattie for International Critical Tables. (The McGraw-Hill Book Company Inc., New York.)

TABLE 15.—APPROXIMATE SPECIFIC GRAVITIES OF SOLUTIONS CONTAINING FERROUS CHLORIDE AND CALCIUM CHLORIDE AT 25°C. (77°F.)

N	Calcium chloride, $CaCl_2$		Ferrous chloride, $FeCl_2.4H_2O$	
	g./l.	oz./gal.	2 *N*. 200 g./l. or 27 oz./gal.	3 *N*. 300 g./l. or 40 oz./gal.
1	56	7.5	1.15	1.21
2	111	14.9	1.19	1.24
3	167	22.4	1.23	1.28
4	222	29.8	1.27	1.31
5	278	37.2	1.30	1.35
6	333	44.7	1.34	1.39

Table 16.—Densities of Commercial Acids

Name	Formula	Concentration, per cent by wt.	Sp. gr.	°Bé.	Wt. of 1 gal., lb.	Pounds of pure acid in each gallon of concentrated acid
(Water).....	H_2O	100	1.00	0.0	8.3	
Acetic.....	$HC_2H_3O_2$	60	1.07	9.5	8.9	5.3
Hydrofluoric.....	HF	48	1.15	19	9.6	4.6
Hydrochloric....	HCl	35	1.18	22	9.8	3.4
Nitric.....	HNO_3	67	1.41	42	11.9	8.0
Sulphuric.....	H_2SO_4	93	1.84	66	15.4	14.3

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